

UC-NRLF



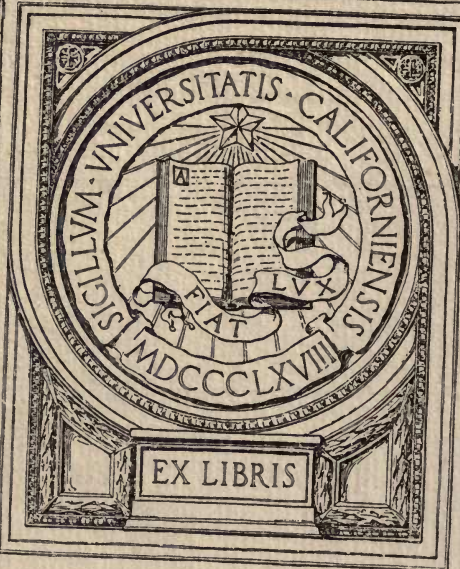
5B 568 025

QC

175

P4

EXCHANGE



EX LIBRIS

377

P 51

*Y. Univ.
Theses each*

Compt. of Sci.

THE INFLUENCE OF MOLECULAR CONSTITUTION

UPON THE

INTERNAL FRICTION OF GASES.

BY

FREDERICK MALLING PEDERSEN, E.E., Sc. D.

Instructor in Mathematics in the College of the City of New York.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF SCIENCE IN THE
FACULTY OF SCIENCE, NEW YORK UNIVERSITY,
APRIL, 1905.



New York
D. VAN NOSTRAND COMPANY,
23 MURRAY AND 27 WARREN STREETS.
1906.

THE INFLUENCE OF MOLECULAR CONSTITUTION

UPON THE

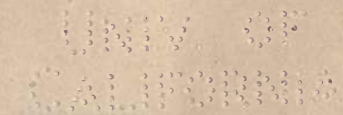
INTERNAL FRICTION OF GASES.

BY

FREDERICK MALLING PEDERSEN, E.E., Sc. D.

Instructor in Mathematics in the College of the City of New York.

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF SCIENCE IN THE
FACULTY OF SCIENCE, NEW YORK UNIVERSITY,
APRIL, 1905.



New York
D. VAN NOSTRAND COMPANY,
23 MURRAY AND 27 WARREN STREETS.
1906.

QC175

P4

NOTICE TO THE PUBLIC

NOTICE

NOTICE

NOTICE

NOTICE

NOTICE

NOTICE

NOTICE

NOTICE

TO THE
PUBLIC

NOTICE

NOTICE

TABLE OF CONTENTS.

	PAGE
INTRODUCTION.....	1-3
HISTORICAL REVIEW.....	3-34
Baily.....	7
Barus.....	29
Bernoulli.....	3
Bessel.....	6
Bestelmeyer.....	33
Boltzmann.....	28
Braun & Kurz.....	24
Breitenbach.....	32
Chézy.....	6
Clausius.....	9
Couette.....	28
Coulomb.....	5
Couplet.....	4
Crookes.....	23
De Heen.....	28
Du Buat.....	4
Euler.....	4
Eytelwein.....	5
Gerstner.....	5
Girard.....	6
Girault.....	10
Graham.....	8
Green.....	7
Grossman.....	24
Guthrie.....	17
Hagen.....	7
Helmholtz & Pietrowski.....	10
Hoffmann.....	25
Holman.....	17
Houdaille.....	31
Jaeger.....	31
Job.....	32
Klemencic.....	24
Kirchhoff.....	17
Koch.....	24
Koenig.....	27
Kundt & Warburg.....	15

	PAGE
Kleint.....	33
Lampe.....	28
Lampel.....	28
Lang.....	13
Ludwig & Stefan.....	9
Marian.....	5
Margules.....	23
Markowski.....	33
Maxwell.....	9
Mathieu.....	10
Meyer, L.....	12, 19, 22
Meyer, L. & Schumann.....	20
Meyer, O. E.....	11, 13, 14, 28
Meyer & Springmühl.....	14
Naumann.....	12
Navier.....	6
Noyes & Goodwin.....	30
Newton.....	3
Obermayer.....	16
Ortloff.....	30
Pérot & Fabry.....	31
Poiseuille.....	8
Poisson.....	7
Prony.....	5
Puluj.....	15, 17, 18
Rayleigh.....	32
Reynolds, F. G.....	33
Reynolds, O.....	25
Sabine.....	6
Schneebeli.....	27
Schultze.....	32
Schumann.....	26
Stefan.....	18
Steudel.....	21
Stewart & Tait.....	11
Stokes.....	9
Sutherland.....	29
Tomlinson.....	27
Warburg.....	16
Warburg & Babo.....	24
Wiedemann, E.....	17
METHOD EMPLOYED IN EXPERIMENTAL INVESTIGATION.....	34
GENERAL DESCRIPTION OF APPARATUS.....	34
APPARATUS NO. 1.....	38
Internal Friction of Air, Apparatus No. 1.....	39
APPARATUS NO. 2.....	40
Internal Friction of Air, Apparatus No. 2 and No. 3.....	42
PREPARATION OF ETHERS.....	42
Internal Friction of Ethers, Apparatus No. 2.....	43

	PAGE
APPARATUS No. 3.....	45
Internal Friction of Ethers, Apparatus No. 3.....	46
MOLECULAR VOLUMES.....	48
MOLECULAR MEAN SPEEDS, FREE PATHS, AND COLLISION FREQUEN- CIES.....	50, 51
COMPARISON WITH THE RESULTS OF OTHERS.....	51
SUMMARY OF RESULTS.....	52
BIBLIOGRAPHY.....	54-59

REPORT OF THE
COMMISSIONER OF THE
BUREAU OF LANDS
AND MINES
FOR THE YEAR
1900
CONTAINING
A SUMMARY OF THE
LANDS AND MINES
IN THE
UNITED STATES
AND TERRITORIES
UNDER THE
MANAGEMENT OF THE
BUREAU OF LANDS
AND MINES
FOR THE YEAR
1900

THE INFLUENCE OF MOLECULAR CONSTITUTION UPON THE INTERNAL FRICTION OF GASES.

BY FREDERICK M. PEDERSEN.

INTRODUCTION.

The effect of molecular structure upon the physical properties of matter has interested many scientists, but much about this question yet remains to be learned. In the hope of making a contribution to the subject the following investigation was undertaken.

A careful historical research reveals the fact that the internal friction of most of the isomeric ether gases that I have employed has never before been determined. Nevertheless, my object has been, not so much to determine with great accuracy the absolute values of these frictions, as to obtain by an extremely sensitive method accurate comparative results, in the hope of proving that difference in molecular constitution is accompanied by measurable difference in friction, and therefore by a difference in the size of the molecule.

By the internal friction or viscosity of a gas, is meant the friction between two adjacent layers of the gas, which are moving in parallel directions but not with the same velocity. It is proportional to the relative velocity and the area of contact of the two layers. The coefficient of internal friction is the constant factor, depending upon the kind of gas under consideration, which, when multiplied by the difference in velocity, gives the friction per square unit of surface of contact of the two layers.

Although there is no sensible cohesion between the particles of a gas, as there is in liquids and solids, the tendency of a moving layer of gas to impart its own velocity to a layer in contact with it, has been satisfactorily explained according to the kinetic theory of gases. As is well known, all the mole-

cules of a gas are supposed to be constantly in rectilinear motion, rebounding in straight lines with undiminished velocity, after collision with one another or a solid wall. In virtue of its mass and velocity each molecule possesses momentum. When one layer of gas is moving over another, there is a constant passage of molecules from each layer into the other. There is then an interchange of momentum, the result being a tendency to equalize the velocities of the two layers. We see thus that the effect of friction is produced between two layers of gas which are not moving with the same velocity in the same direction.

It has been demonstrated¹ that the coefficient of friction of a gas,

$$\eta = \frac{m G}{4 \pi s^2}$$

where m = the mass of a molecule, G = the mean value of the velocity as deduced from the mean kinetic energy, and s = the distance between the centres of two molecules at impact, or the diameter of the sphere of action. This formula brings out the remarkable and very important law, that the viscosity of a gas is independent of the pressure at a constant temperature. It also shows that the smaller the sphere of action, the greater will be the coefficient of viscosity. We also see that the viscosity varies directly as the rectilinear velocity of the molecules, *i.e.*, as the square root of the kinetic energy, and therefore as the square root of the absolute temperature, since the last two are directly proportional to each other. The first named law has been found true experimentally for all ordinary pressures, but the last law connecting the viscosity and absolute temperature has not been substantiated by experiment. This disagreement between theory and practice I will leave for a fuller discussion later, merely noting in passing that Maxwell² has shown that the assumption in regard to the nature of the impact between two molecules determines the relation between the coefficient of friction and the absolute temperature.

That the coefficient of friction of a gas is independent of the pressure seems at first inconceivable, but it can probably

1. O. E. Meyer's Kinetic Theory of Gases, 1899, p. 179.

2. Phil. Mag., 1868 (4), Vol. 35, p. 211.

be better understood by a consideration of another formula which has been deduced from the kinetic theory, viz.: $\eta = 1/3 d G L^1$ where d is the density, G is square root of the mean square of velocity, and L is the mean free path of a molecule. It can be shown that L and d are inversely proportional to each other so that their product is constant, and therefore η is thus independent of a change in density.

Before describing my own experimental investigations I will give a historical review of the work done by previous experimenters in the subject of the viscosity of gases. Methods of research in this line seem to have developed out of or along with investigations in the subject of the internal friction of liquids. I shall therefore frequently have occasion to refer to this last named subject, but I shall make no attempt whatever to follow out its complete development.

HISTORICAL REVIEW.

O. E. Meyer² points out that Newton³ made the first attempt at a theory of the friction of fluids. His fundamental hypothesis was that the friction between two adjacent layers of a fluid is proportional to the difference of velocity, the area of contact and independent of the pressure. This hypothesis has several times since been enunciated by others, independently of Newton, and used as a basis for a theory of fluid friction. Unfortunately Newton's mathematical development of the theory from this assumption is erroneous. His experiments, like those of many early investigators, seem to have been confined to observations of pendulums. It is interesting to note that on searching for the resistance which air opposes to the movement of a globe, swinging in very small arcs, he used a formula composed of three terms: one containing the square, the second the $3/2$ power and the third the first power of the velocity.⁴ Later, 1719, in calculating the resistance which is offered to spheres falling slowly in air or water, he reduced the formula to two terms: one varying as the square of the velocity, and the other constant.

Bernoulli⁵ pointed out Newton's error in his paper before

1. Meyer's Kinetic Theory of Gases, 1899, p. 178.

2. Crelle's *Journal für Mathematik*, 1861, Bd. 59, p. 229.

3. *Philosophiæ naturalis principia mathematica*, 1687, Lib. II., Sec. IX.

4. *Principia* Lib. II., Prop. XL.

5. *Opera Omnia*. Lausanne et Genevæ 1742. Tomus III. Nouvelles pensées sur le système de M. Descartes, XIX.-XXIII.

the French Academy in 1730, explaining the orbits of the planets and the precession of the equinoxes, according to the Cartesian vortex hypothesis. On submitting to calculation the experiments with pendulums made by Newton, Bernoulli supposes only two terms to represent the resistance; one varying as the square of the velocity, the other constant. He points out that the theory does not agree with the experiments, but states that we cannot conclude anything from that because of the difficulty and delicacy of the observations necessary.¹

Couplet,² in 1732, called attention to the fact that the rules then in use for determining the flow of water through pipes were utterly useless, as the error amounted to nearly 100%. He made some experiments on a large scale at Versailles, and found that the water delivered was frequently $1/20$ or $1/30$ what was promised by his calculations. Nothing was known about internal friction, the effect of bends, diameter of pipe, etc. Couplet apparently made no attempt to discover the true laws of flow and seemed to scarcely believe in the possibility of discovering them.

Euler³ in 1756 fell into the error of supposing that the friction of a liquid is independent of the velocity and proportional to the hydrostatic pressure.

Du Buat⁴ 30 years later made a series of quite elaborate experiments with pendulums consisting of spheres of lead, wood and paper, which he oscillated in water and air. He noted that similar laws seemed to hold in both media. He noticed that both liquid and air were dragged along by the spheres. He found the resistance to the motion of the spheres was proportional to their surfaces, and that the resistances of air and water are as their densities. He calculated the resistance of the air to Newton's falling spheres, and found that up to a velocity of 23 feet per second the resistance is as the square of the velocity. At higher velocities he showed it was greater owing to a constant vacuum back of the ball. He pointed out a double correction which must be applied to a pendulum in reducing the results to a vacuum. 1° for its apparent loss in weight owing to the buoyancy of the air,

1. Mémoires de Petersbourg. Tome III. and V.

2. Mémoires de l'Académie, 1732.

3. Tentamen theoriæ de frictione fluidorum. Novi Petropolitani, Tomus VI., 1756; 7 Pag. 338.

4. Principes d'Hydrauliques, 1786, Vol. 2, Part 3; Sec. 2, p. 279.

and 2° for the increase in the moment of inertia due to the air clinging to it. A full discussion and analysis of his work with pendulums was given by Professor Stokes¹ in 1850.

Some years previous to Du Buat's work Mairan² made quite an important advance in the experimental study of pendulums by the invention of the method of coincident observations of two pendulums, a method made use of by many later investigators.

Gerstner,³ through experiments made in Prague in 1796, discovered the very great effect which temperature has upon the mobility of water. He found that in many cases a rise of 20 or 30 degrees in temperature doubled the quantity of liquid delivered through narrow tubes, thus showing a very marked decrease in the internal friction of the water.

Coulomb⁴ in 1801 published an account of experiments undertaken to determine the cohesion of fluids and the laws of their resistance when in very slow motion. He claims that the expression for the resistance of a fluid has two terms, one proportional to the square of the velocity, and the other to its first power, and that if there is a constant term, it is so small in all fluids of small cohesion, that it is almost impossible to appreciate it. Instead of using the pendulum method, he noted the diminution in amplitude of oscillation of horizontal disks, oscillating in their own plane under the torsion of a brass wire. He was the first one to adopt this important method which has since been employed by many others.

Both Prony⁵ in 1804, and Eytelwein⁶ ten years later, developed theories of the flow of water through pipes, but with the temperature left entirely out of consideration. Prony found the loss of head per unit length is very nearly proportional to the square of the mean velocity of the water. He proposed the formula: $1/4 D j = \alpha v + \beta v^2$ where D = diameter of the pipe, j = the fall per metre, v = velocity, $\alpha = 0.0000173314$, $\beta = 0.0000348259$.

1. Cambridge Phil. Trans., 1856, Vol. 9, Part 2, p. 8.

2. Historie de l'Acad. de Paris, 1735, p. 166.

3. Gilbert's Annalen, Bd. 5, 1800, p. 160. Neu. Abh. der kön. Böhm. Gesell. der Wiss., Bd. 3, Prag. 1798.

4. Mem. de l'Institut Nat. des Sciences et Arts. Année 9, Tome III., p. 246.

5. Recherches Physico-mathém. sur la Théorie des Eaux Courantes, Paris, 1804.

6. Abh. d. Berl. Akad., 1814 and 1815.

Girard¹ in 1815 investigated the flow of liquids through capillary tubes of copper with special reference to the effect of temperature. He found that at 86° C. four times as much water was delivered as at 0° C. He noted that when the capillary reached a certain length the term which is proportional to the square of the velocity disappears from the formula for the uniform motion of liquids. In fine tubes he found the loss of head per unit length very nearly proportional to the velocity of flow. He refers to the work of Chézy² in 1775 as being the first investigation of the flow of water in aqueducts.

In 1823 Navier³ deduced the differential equations of the motion of a viscous medium from considerations which are analogous to those he employed for the derivation of the differential equations of the phenomena of elasticity. He treats of the movement of a fluid in a straight pipe of circular cross section. In a later paper he discusses the discharge of air from pipes and orifices, and endeavors to take into account the effect of bends. The velocity of flow seems to have been his chief concern. The smallest pipe he used had a diameter of 1.579 cm.

In 1826 Bessel⁴ published the result of his classical investigation of the length of the simple second's pendulum. His method consisted in the comparison of two pendulums whose difference in length was exactly one toise or 1.92 metres. He took account of the effect of the resistance of the air and showed that the old correction for reduction to a vacuum was in error and determined its correction factor, viz.: $k = 1.946$ for a sphere about 5 cm. in diameter.

Sabine⁵ made the interesting experiment in 1829 of swinging a pendulum in air under a pressure of about half an atmosphere, and in hydrogen at atmospheric pressure, and found that hydrogen had a much greater resistance in proportion to its density than had air. He correctly ascribed the cause to an inherent property of elastic fluids, independent of their density, analogous to that of viscosity of liquids. He also investigated the correction for reduction to a vacuum. His pendulum

1. Mém. de l'Institut, Classe Sc. and Math., 1813-15, p. 248; 1816, p. 187.

2. Mém. manuscrit de l'Ecole des Pons et Chaussées, 1775.

3. Mém. de l'Acad. Roy. des Sciences, 1823, Tome 6, p. 389, 1830, Tome 9, p. 311.

4. Abh. Berl. Akad. Math. Klasse, 1826, p. 1.

5. Phil. Trans., 1829, p. 207 and 331; 1831, p. 470.

made 10.36 more oscillations in a given time in a vacuum than in air, whereas calculations showed that it ought to make only 6.26 more, hence the correction for reduction to a vacuum was in error.

In 1829, Poisson¹ derived, by a method similar to Navier's, the differential equations of equilibrium and motion of fluids. Two years later he wrote a paper on the motion of a pendulum in a resisting medium, in which he discusses the correction for reduction to a vacuum and infinitely small arcs, and reviews the work of Du Buat, Bessel and Sabine.

In 1832 Baily² made a very thorough and systematic study of the correction of a pendulum for the reduction to a vacuum. He oscillated 86 different pendulums with bobs of various materials, sizes and shapes in air and then in a vacuum. In the case of a spherical bob two inches in diameter he found the old correction should be multiplied by 1.748 which agrees quite well with Bessel's value of k but not so well with Du Buat's, 1.585. He found the correction varies with the shape but not with the specific gravity of the pendulum.

Green,³ continuing researches on the vibration of pendulums in fluid media, claimed that in the case of a sphere the density of the pendulum should, in the calculations, be augmented by one half the density of the surrounding fluid, while its weight is diminished by the weight of the volume of the fluid it displaces.

Hagen,⁴ returning in 1839 to the investigation of the flow of water in small cylindrical tubes, tried to improve on Prony's and Eytelwein's equations by taking account of the temperature. He criticized Du Buat for not recording the temperature in any of his experiments in spite of the fact that he knew warm water is more fluid than cold water. Hagen found the rapidity of flow increases with the temperature to a maximum, then diminishes for a rise of 10 or 20 degrees, and then begins to increase again. With large tubes and high speeds both turning points fell below the freezing point. With very narrow tubes and low speeds they both fell above the boiling point.

1. Journal de l'Ecole Polytech., 1831, Tome 13, p. 139. *Connaissance des Temps*, 1834, Appendix. *Mém. de l'Acad.*, 1832, Tome 2, p. 521.

2. *Phil. Trans.*, 1832, Part 1, p. 399.

3. *Trans. Royal Soc. Edin.*, Vol. 13, 1836, p. 54.

4. *Pogg. Ann.*, 1839, Bd. 46, p. 423. *Abh. d. Berl. Akad.*, 1854, p. 17.

In the following year Poiseuille¹ published the results of his epoch-making experimental research on the movement of liquids in tubes of very small diameter. He used glass capillaries from 0.013 mm. to 0.652 mm. in diameter, and from 2 to 800 mm. long. They were slightly elliptical in cross section, so he took the mean diameter. The liquid, water or alcohol, was contained in a bladder and pressed out through the capillary. He investigated the effect on the quantity of liquid discharged, of the pressure, length of tube and the temperature. He found the volume of liquid discharged varies directly as the pressure, inversely as the length of tube, directly as the fourth power of the diameter, and with the temperature according to an empirical law. He found the value of a certain factor to be constant for all sizes of tubes. This factor for water was 1836.7 at 0° C. and 2495.9 at 10° C.

What Poiseuille had done for liquids, Graham² did for gases a few years later. He first investigated the effusion of gases into a vacuum through a very fine aperture in a thin plate, and found the velocity of effusion varies inversely as the square root of the density of the gas. He determined the effusion coefficients of a number of gases referred to air and oxygen as unity. On the other hand, on causing gases to transpire through capillary tubes which were long in comparison with their diameter, he discovered the transpiration coefficients to be independent of the density of the gases. He either let the gas flow from a gas holder through the capillary into a partial or complete vacuum, or from a compression cylinder into the air. In both cases the pressures were not constant during the experiment. He found the velocities of transpiration to vary directly as the pressure, and inversely as the length of tube. A rise in temperature he found decreased the velocity. The transpiration rate was independent of the material of the capillaries, which were of glass or copper. The presence of moisture in the air had but a small effect upon its transpiration. The velocities with which the different gases passed through

1. Soc. Philomath, 1838, p. 77, Comptes Rendus, 1840, Vol. II., pp. 961, 1041. 1841, Vol. 12, p. 112; 1842, Vol. 15, p. 1167. Ann. de Chim. et de Phys. 1843 (3), Vol. 7, p. 50. Mém. de Savans étrangers, 1846, Vol. 9, p. 433.

2. Phil. Trans., 1846, Vol 136, p. 573. Phil. Trans., 1849, Vol. 139, p. 349.

the various capillaries, bore a constant relation to each other. The compounds of methyl had a less velocity than the corresponding compounds of ethyl, but a constant relation appeared between them.

In 1849 Stokes¹ published an elaborate mathematical treatment of the theories of the internal friction of fluids in motion, and derived the same complete equations of motion as Navier and Poisson by a different method. The following year he read a paper "On the Effect of the Internal Friction of Fluids on the Motion of Pendulums" in which he gave a very full discussion of the work of Du Buat, Bessel and Baily already referred to. He was well aware of the fact that the air sticks fast to a pendulum, which therefore in its oscillations causes a friction of air on air. He was in error, however, in thinking that what we now know as the coefficient of friction was dependent upon the density. From his own experiments and those of others, he deduced values of what he calls the "index of friction," which is our coefficient divided by the density. He found his results agreed well with Baily's but not with Bessel's. Baily's experiments show η for air to be = .000104 in c.g.s. units. Stokes also deduced the index of friction of water from Coulomb's observations on the decrement of the arc of rotary oscillation of horizontal disks.

Ludwig and Stefan² in 1858 called attention to the formation of eddies when a tube discharges liquid into one of larger bore, thus causing an increase in resistance. A similar action was later shown to take place in a gas under the same circumstances.

The same year Clausius³ published his important paper on the kinetic theory of gases which did so much to establish that theory.

In 1860 Maxwell⁴ entered this field of investigation and made some important contributions to the kinetic theory of gases, proving mathematically that η must be independent of the density. Six years later appeared his Bakerian Lecture in which he gave an account of his experiments on the

1. Trans. Camb. Phil. Society, 1849 (3), Vol. 8, p. 287. Trans. Camb. Phil. Society, 1856, Vol. 9, p. 8. Phil. Mag., 1851 (4), Vol. 1, p. 337.

2. Sitzber. Wien. Akad., 1858, Vol. 32, p. 25.

3. Pogg. Ann., 1858, Bd. 105, p. 239.

4. Phil. Mag., 1860 (4), Vol. 19, p. 31; 1869 (4), Vol. 35, p. 209, 211. Phil. Trans., 1866, Vol. 156 (1), p. 249. Collected Papers, Vol. II. Proc Royal Society, 1866, Vol. 15, p. 14.

viscosity of air and other gases. His method was a modification of Coulomb's, in which he used several oscillating disks with stationary plates between them. The only uncertainty in his mathematical treatment of the theory of his apparatus is due to the action which takes place at the edges of the oscillating plates which is not fully understood. His value for η for air at 18° C. is .0002.

He found from his experiments that the coefficient of friction was directly proportional to the absolute temperature instead of to the square root of the latter. He then modified his kinetic theory of gases in order to make the theory agree with his observations, by adopting the hypothesis of a repulsive force between the molecules, which varies inversely as the fifth power of the distance between them, this being the only law of force which causes η to increase as the first power of the absolute temperature. His observations concerning the increase of η were undoubtedly in error as other investigators do not agree with him.

Helmholtz and Pietrowski¹ in 1860 tried an interesting modification of Coulomb's method which consisted in observing the logarithmic decrement of the rotary oscillations of a spherical vessel containing the liquid under investigation. Helmholtz worked out the mathematical theory of this method while Pietrowski performed the experiments. With the interior surface of the vessel highly polished and gilded a slipping of the fluid along the side of the vessel was thought to be observed. The results are to Poiseuille's as 4:5. Probable sources of error mentioned are vibrations and changes of temperature.

Girault² in his pendulum experiments of that year brought out the fact very clearly that most of the resistance to a pendulum's motion resides at the bob and not at the point of suspension.

In 1863 Mathieu³ deduced Poiseuille's law for capillaries of elliptical cross section. Poiseuille found

$$Q = K \frac{\text{Pressure} \times \text{Diameter}^4}{\text{length}}$$

where Q is the quantity of liquid discharged in a unit time

1. Wien. Ber. Mathm. Naturw., 1860, Vol. 40, p. 607.

2. Mém. de l'Acad. de Caen, 1860.

3. Compt. Rend., 1863, Tome 57, p. 320.

and K is a constant depending upon the nature of the liquid. Mathieu supposes the velocity of the liquid in contact with the capillary wall to be zero, because K is independent of the material of the capillary, and because of observations on blood in the capillaries of a frog's foot. For round capillaries he gives

the above equation the form $Q = \frac{\text{Pressure } R^4}{8 N \text{ length}}$ where N is a

constant depending upon the liquid. For elliptical capillaries

$Q = \frac{P a^3 b^3}{4 N l (a^2 + b^2)}$ where a and b are the semi-major and minor axes of the ellipse.

In 1865 Stewart and Tait¹ made some interesting observations on the heating of a disk rotating rapidly in vacuo. They found the heating independent of the rarefaction which seemed to show the friction independent of the density or pressure.

O. E. Meyer,² who probably did more than any other one man to advance our knowledge of the viscosity of gases, began investigations in this subject about this time. A few years before he had begun the study of the viscosity of liquids, but he now turned his attention to gases. He first adopted the oscillation method of Coulomb and found a value of η for air at 18° C. of 0.00036 which is much too large. Later he pursued his investigations with pendulums. His object was to determine what effect pressure and temperature have on the coefficient of friction of air. He found that the rarefied air in a supposed vacuum has a noteworthy effect on a pendulum. He therefore questioned the reliability of Baily's and Sabine's results. Bessel's work he considered much better. From it he calculated η for air = .000275. His own observations gave $\eta = .00027$ to .00052. By varying the pressure and temperature he concluded that with diminishing pressure η decreases, but less rapidly than the density, and with rise of temperature η increases an insignificant amount, whereas Maxwell claimed it rises 2% for each 10° C. which is not so far from the truth.

The following year in order to check his own results, O. E. Meyer³ calculated coefficients of friction from Graham's ob-

1. Proc. Royal Society, 1865, Vol. 14, p. 339. Phil. Mag. (4), Vol. 30, p. 314.

2. Crelle's *Journal für Math.*, 1861, Bd. 59, p. 229. Pogg. Ann., 1861, Bd. 113, p. 55. 1865, Bd. 125, pp. 177, 401, 564.

3. Pogg. Ann., 1866, Vol. 127, pp. 253, 353.

servations, although he believed that for absolute measurements Coulomb's method was superior to Graham's, because in the former external friction is eliminated, it being settled that the gas adheres to the oscillating disks. For the transpiration method he derived the formula:

$$\eta = \pi t \frac{p_1^2 - p_2^2 R^4}{2 p_1 V_1 8 L} \left(1 + 4 \frac{\zeta}{R}\right)$$

in which t is the time; p_1 is the pressure of the gas entering the capillary; p_2 is the pressure of the gas leaving the capillary; V_1 is the volume of the transpired gas measured at the pressure p_1 ; R is the radius of the capillary; L is its length; ζ is the coefficient of slip of the gas on the walls of the capillary. The term $4 \frac{\zeta}{R}$ is so small compared with 1 that most

investigators until very recently have neglected it. He found η for air at about 15° C. = 0.000178 to 0.000206 from Graham's experiments. He was fully convinced by this time that η is almost, if not absolutely, independent of the pressure, but he was not certain of the law in accordance with which η increases with the temperature.

In 1867 Lothar Meyer¹ published his calculations of the molecular volumes as derived from his brother's determinations of η . He derived the formula:

$$v = C \sqrt{\left(\sqrt{\frac{m}{\eta}}\right)^3}$$

in which v = molecular volume; C = a then not obtainable constant which is the same for all gases at the same temperature; m = molecular weight of the gas. He showed that the ratio of the molecular volumes of two substances is about the same as the ratio of their molecular volumes as determined by Kopp² from their boiling points.

Naumann,³ working on the same lines that year, derived the formula $\frac{r^2}{r_1^2} = \frac{\eta_1}{\eta} \sqrt{\frac{m}{m_1}}$ which r and r_1 are in the radii of spheres of action, and m and m_1 are the molecular weights of two sub-

1. Ann. d. Chem. u. Phar., 1867, Suppl. Bd., 5, p. 129.

2. Ann. d. Chem. u. Phar., 1855, Bd. 96, pp. 1, 153, 303.

3. Ann. d. Chem. u. Phar., 1867, Suppl. Bd. 5, p. 252.

stances. He showed the methyl ether molecule to be 9 times the volume of a hydrogen molecule.

In 1871 O. E. Meyer¹ returned to the observations of pendulums and made some careful experiments with pendulums varying in length from 14.5528 to 4.6868 metres, which were set up in the stairway of the University of Breslau. He found η for air at 18° C. to be 0.000216 to 0.000233.

Recognizing that Maxwell's modification of Coulomb's method was superior to his own, which gave only the $\sqrt{\eta}$ instead of η , and was less sensitive than Maxwell's owing to the absence of stationary plates between the oscillating ones, Meyer² proceeded now to repeat Maxwell's experiments. In order to avoid irregularities in the internal friction of a single wire he adopted bifilar suspension. He found η for air at 18° C. = 0.000190 to 0.000197 which he considered good agreement with Maxwell's value 0.0002. In accordance with these more correct values of the coefficient of viscosity of air he revised his list of η for other gases and gave to methyl ether the value of 0.000107 at 15° C.

During that same year Lang³ published the results of some experiments on air and other gases, using the transpiration method. His apparatus was extremely simple, the gas being sucked through a capillary by a falling column of water. His capillaries were of glass, one of round and another of elliptical cross section. The round capillary gave η for air at 15° 0.000168 to 0.000178; the elliptical one gave at 9° 0.000143 to 0.000148. The discrepancy between the results of the two capillaries Meyer suggested might be partly owing to the fact that perhaps the cross section of the elliptical one was not a true ellipse.

Having already shown theoretically that the volume of gas delivered by a capillary in a unit of time is proportional to the fourth power of its radius, inversely proportional to its length, and directly proportional to the difference in pressure between its two ends, provided the gas is measured at a pressure which is the arithmetical mean between the two terminal pressures, O. E. Meyer⁴ proceeded in 1873 to prove experimen-

1. Pogg. Ann., 1871, Vol. 142, p. 481.

2. Pogg. Ann., 1871, Vol. 143, p. 14.

3. Wien. Ber. Mathem. Naturw., 1871, Vol. 63, 2 Abt., p. 604. Wien. Ber. Mathem. Naturw., 1872, Vol. 64, 2 Abt., p. 487. Pogg. Ann., 1872, Vol. 145, p. 290. Pogg. Ann., 1873, Vol. 148, p. 550.

4. Pogg. Ann., 1873, Vol. 148, pp. 1, 203.

tally this law, whose similarity to Poiseuille's law for liquids is at once evident. He employed several capillaries varying in cross section from .0008 to .0016 sq. cm. Working under the assumption that the air adheres so firmly to the walls of the capillary that there is no slipping, he obtained the following values of η for air: 0.000168 at 0° C., 0.000184 at 14.4° C., 0.000197 at 21.1° C.

The above experiments were made by causing the air to transpire from one copper vessel through the capillary into another similar vessel, allowing the pressure but not the volume of the air to change. He next repeated the experiments by allowing the volume but not the pressure to change by employing constant water suction. He found η at 10° C. to be .000192 — .000199 and at 100° C. $\eta = .000211 - .000218$. His results do not agree with Maxwell's in showing η to vary as the absolute temperature, neither do they agree with theory in proving η to vary as the square root of the absolute temperature. His results are midway between Maxwell's and the theory, viz., η varies as the $3/4$ power of the absolute temperature. He proposed the formula:

$$\eta = \eta_0 (1 + 0.0024 T)$$

in which $\eta_0 = 0.000171$ and $T =$ temperature in C°. Maxwell's formula was $\eta = \eta_0 (1 + 0.003665 T)$.

Using a still smaller capillary whose cross section was .00015 sq. cm. through which he sucked the air by means of a mercury pump he found η at 22° C. to be .000187 and at 100° C. .000223 — .000227. He then modified his formula to read $\eta = 0.000174 (1 + 0.003 T)$.

Repeating Maxwell's oscillation experiments once more with bifilar suspension Meyer found $\eta = .000190 (1 + 0.0025 T)$ which is in fairly good agreement with his transpiration results, so that Meyer concludes Maxwell's results are in error owing to the heating of the suspension wire and the poor position of the thermometer with reference to the oscillating disks. Meyer accounts for the difference between his own results and theory by the fact that heat increases not only the rectilinear velocity of the molecules but also the internal movements of the atoms which build up the molecules.

A little later Meyer and Springmühl¹ using the same apparatus obtained the coefficients of friction of 19 different gases, some

1. Pogg. Ann., 1873, Vol. 148, p. 526.

of which had been investigated by Graham, with whom they agreed within 2 to 20%. Their values for air and methyl ether were .000190 and .000102 at 15° C.

No difference in η was observed when transpiration took place into a vessel filled with the same kind of gas or with a different gas, showing that there was no diffusion back through the capillary. This proves that a gas has the same pressure upon another kind of gas as upon the same kind as itself.

The following year Puluji¹ investigated the coefficient of internal friction of air as a function of the temperature, using a transpiration apparatus like Professor Lang's. He maintains that the loss of heat due to the expansion of the air in the capillary is compensated for by the heat which the air receives from the walls of the capillary. He found η for air at 15° C. = 0.00018526. For a temperature range from 13.4° C. to 27.2° he found η to vary according to the formula $\eta = \eta_0 (1 + 0.003665 T)^{0.652776 \pm 0.020893}$.

After enlarging the temperature range from 1.5° C. to 91.2 he found the exponent of the above parenthesis changed to 0.590609 ± 0.009510 .

Kundt and Warburg² published in 1875 an important investigation which proves that the law that η is independent of the pressure does not hold for extremely small pressures. They used Coulomb's method, employing only one oscillating glass disk with bifilar suspension. For air at 15° C. they found $\eta = 0.000189$ and for pure aqueous vapor at 15° C. and a tension of about 16 mm. $\eta = .000099$.

They found that with air the logarithmic decrement began to diminish at a pressure of $2\frac{1}{2}$ mm. of mercury, and fell off very perceptibly at a pressure of $\frac{1}{2}$ mm. This diminution was ascribed to a slipping of the air on the surface of the oscillating disk. From their work they concluded that the coefficient of slip for a gas on a solid partition has sensibly a determined value dependent upon the nature of the gas, so long as the latter is present in layers thicker than 14 times the mean length of molecular path, and it is inversely proportional to the pressure. The absolute value, which is the coefficient of internal

1. Wien. Ber. Mathm. Naturw., 1874, Vol. 69 (2), p. 287. Wien. Ber. Mathm. Naturw., 1874, Vol. 70 (2), p. 243.

2. Monatsber. d. Berl. Akad., 1875, p. 160. Pogg. Ann., 1875, Vol. 150, pp. 337, 525. Phil. Mag., 1875 (4), Vol. 50, p. 53.

friction divided by the coefficient of external friction of the gas, they found from experiment to be for air $0.0001 \frac{760}{p}$ whereas

theory showed it ought to be $0.000058 \frac{760}{p}$ where p = pressure expressed in mm. of mercury.

Warburg¹, pursuing the same subject further the following year, proceeded to find the coefficient of slip for air by the transpiration method. He pointed out that because the radius of a capillary is smaller than we can make the distance between oscillating plates, the effect of slipping in transpiration experiments is noticeable at higher pressures than in the method of oscillations. Using a pressure of 38 mm. of mercury and a capillary of 0.15 mm. radius he found η for air was 5% smaller than it ought to be, owing to slipping. The temperature exponent from 0° to 100° C. he found to be 0.77 which is in good agreement with O. E. Meyer. His temperature exponent for hydrogen is 0.63. He gives the formula:

$$\frac{\text{True } \eta}{\text{Observed } \eta} = 1 + \frac{4\zeta}{R} \text{ where } \zeta = \text{coefficient of slip and } R$$

= radius of the capillary.

Obermayer's² results agree with those of O. E. Meyer in showing that η for air increases as the $3/4$ power of the absolute temperature. He used the transpiration method and pointed out two possible sources of error inherent in this method: 1st. the clinging of a layer of air to the inside wall of the capillary which diminishes the cross section more at low than at high temperatures; 2nd. the change in temperature which the gas undergoes in the capillary as it expands from the entering to the terminal pressure.

He carried the temperature as high as 270° C. and criticized Puluji for his small temperature range. His absolute values of η are lower than those of Meyer. He points out that the so-called permanent gases are distinguished by a temperature

1. Pogg. Ann., 1876, Vol. 159, p. 379.

2. Wien. Ber. Mathem. Naturw., 1875, Vol. 71 (2), p. 281. Wien. Ber. Mathem. Naturw., 1876, Vol. 73 (2), p. 433. Carls Rep., 1876 (2), Vol. 12, pp. 13, 456. Carls Rep., 1877, Vol. 13, p. 130. Phil. Mag., 1886, Vol. 21.

exponent of $3/4$, whereas the coercible gases have this exponent almost unity.

E. Wiedemann¹, assuming as did several predecessors that the variation of η with the temperature can be expressed by the formula $\eta = \eta_0 (1 + \alpha T)^n$, proceeded to determine the exponent n , which I call the temperature exponent, for several gases. He adopted the transpiration method, driving the gas through the capillary by the pressure produced by mercury flowing from a reservoir. His capillary was surrounded by cold water, steam or aniline vapor, so that his temperature range was from 0 to 184.5° C. He assumed that the absolute value of η for air had already been determined with sufficient accuracy by Meyer, Maxwell, Kundt, Warburg and others, so that he gave only comparative results. He found the temperature exponent, n , to vary with different gases but in different ways. With most gases he tried, it decreased with higher temperatures. Thus for air from 0° to 100° C. it was .7333 and from 100 to 184.5 it was only .6701. For CO it was .6949 from 0° to 184.5° C.

Puluj² with a modified Coulomb apparatus consisting of an oscillating disk of thin mirror glass between two fixed disks of thick plate glass, found the temperature exponent for air = 0.72196 ± 0.01825 which agrees pretty well with Meyer and Obermayer but not with his own previous results.

Kirchhoff³ in 1877 gave a complete mathematical deduction of the formulæ to be used in calculating the coefficient of friction of a gas from the logarithmic decrement of a sphere oscillating about a diameter and for an ellipsoid of revolution rotating about an axis of symmetry.

Holman,⁴ in a series of very careful experiments by the transpiration method, found that η for air increases as the 0.77 power of the absolute temperature. Later experiments at higher temperatures showed that the increase of η falls off in rate as the temperature rises, except possibly in the case of hydrogen, which he therefore regards as our most perfect gas.

Guthrie⁵ in order to determine whether there were any

1. Archiv. d. Sc. Phys. et Nat. de Genève, 1876, Vol. 56, p. 277
Fortschr. d. Phys., 1876, Vol. 32, p. 206.

2. Wien. Ber. Mathem. Naturw., 1876, Vol. 73 (2), p. 589.

3. Mechanik, 1877, 4 Aufl., 26 Vorl., p. 383.

4. Proc. Am. Acad., Boston, 1877, Vol. 12, p. 41; 1886, Vol. 21, p. 1.
Phil. Mag., 1877 (5), Vol. 3, p. 81; 1886, Vol. 21, p. 199.

5. Phil. Mag., 1878 (5), Vol. 5, p. 433.

disturbances, such as eddies, in the flow of a gas at the beginning and end of a capillary, took the transpiration time of a given volume of air through a capillary, that he afterward cut up into a number of small pieces which he joined together by guttapercha tubing. With the capillary in this condition he found the same transpiration time as before, which seemed to prove the absence of disturbances at the ends of the capillary. A later investigator, Hoffmann, does not agree with him.

Puluj¹ in 1878 attacked the problem of the internal friction of vapors, using the modified Coulomb-Maxwell apparatus already mentioned, with unifilar suspension. From experiments with ether he concluded that its η is independent of the pressure. He found η at $10^\circ = 0.0000716$ and at $37.1^\circ \text{C.} = 0.0000792$. Its variation with the temperature he gives by the equation

$$\eta_T = 0.0000689 (1 + 0.0041575 T)^{0.94}$$

The coefficient of expansion of ether = .0041575 he calculated from Herwig's² data. From this equation he concluded that for ether vapor and probably all vapors η is proportional to the absolute temperature. He also experimented on the vapors of alcohol, chloroform, benzol and acetone. Taking the molecular volume of hydrogen as 1, he found those for ether and alcohol 101.1 and 52.9 respectively, which is in fair agreement with Kopp's³ molecular volumes deduced from the boiling points of the liquids.

Puluj agreed with Stefan⁴ in thinking that each molecule of a gas is surrounded by an envelope of ether, and in explaining the increase of internal friction with rise of temperature, by saying that with increased velocity the molecules on impact penetrate further into one another. His experiments with air at very low pressures led to the result, that while the pressure diminishes from 754 to 0.03 mm., the coefficient of friction only decreases to about one half its value, which proves what a great number of molecules remain in quite high vacuum.

Puluj⁵ next took up the problem of determining the coefficient of friction of a mixture of the two gases CO_2 and H , using

1. Wien. Ber., 1878, Vol. 78 (2), p. 279; Carls Rep., 1878, Vol. 14, p. 573; Phil. Mag., 1878 (5), Vol. 6, p. 157.

2. Pogg. Ann., 1869, Bd. 137, p. 595.

3. Ann. Chem. Phar., 1855, Bd. 96, pp. 1, 153, 303.

4. Wien. Ber., 1862 (2), Vol. 46, pp. 8, 495; 1872 (2), Vol. 65, p. 360.

5. Carls Rep., 1879, Vol. 15, p. 578 and 633.

the same apparatus as for vapors. He drew the conclusions: (1) The coefficient of friction of a mixture of CO_2 and H is not larger (smaller) than the coefficient of that constituent which has the larger (smaller) coefficient; (2) gases with larger molecular weights have in a mixture of equal proportions a greater influence on the value of the coefficient of friction of the mixture.

He proved that Maxwell's formula for the η of a mixture gives too small a value, and proposed another formula which gives η too large, but agrees with experiment in showing the curious fact that with a small percentage of the lighter gas η increases.

In 1879 Lothar Meyer¹ began the study of the internal friction of vapors by the transpiration method. The capillary, which was nearly $1\frac{1}{2}$ metres in length, was coiled into a helix and fastened in the upper part of a boiling flask. The lower end of the capillary passed through the neck of the flask into a condenser. The substance to be examined was boiled at a regulated pressure, the vapor evolved surrounding the capillary and raising it to the same temperature. A part of the vapor, which was of course saturated, entered the upper end of the capillary and passed through it into an air-free cooled space, where it was condensed and measured as a liquid. The volume of the vapor transpired was calculated from the amount of liquid collected in the condenser.

This method is open to criticism for several reasons, one of which is the coiling of the capillary into a small helix, thus possibly deforming its bore and causing additional resistance by the curved path of the gas. The vapor at the boiling point of the liquid can also hardly be regarded as a true gas, and should have been tested at several degrees above boiling. The expansion of the saturated vapor as it passed through the capillary probably also changed its state. Furthermore the great length of time, several hours, needed for transpiration made it difficult to keep conditions constant.

A preliminary test with air gave η at room temperature = 0.000188 which is higher than most other observers have found by the transpiration method. He found η for benzole about 50% higher than Puluj had found, that its increase with rise of temperature is more rapid than for so-called permanent gases. He discovered that with a difference in pressure of

1. Wien. Ann., 1879, Bd., 7 p. 497.

14 cm. of mercury between the two ends of the capillary his apparatus gave η considerably too small. On calculating molecular volumes he found that they are larger, the lower the temperature.

Two years later were published the results of observations made by L. Meyer and Schumann¹ on a very large number of substances, using the transpiration apparatus just described. Two capillaries were employed, one 1427 mm. long and 0.31 mm. in diameter; the other 1404 mm. long and 0.3328 mm. in diameter. The second capillary gave values 3% higher than the first. Below is the table of their results for Esters.

TABLE V. ESTERS $C_n H_{2n} O_2 \quad \eta \times 10^6$.

Acid Radical	Alcohol Radical				
	Methyl	Ethyl	Propyl	Isobutyl	Amyl
	$n=2$	3	4	5	6
Formic Acid	173	156	159	172	160
	$n=3$	4	5	6	7
Acetic Acid	152	152	160	155	
	$n=4$	5	6	7	8
Propionic Acid	150	158	153	164	158
	$n=5$	6	7	8	9
Normal Butyric Acid	159	160	164	167	155
Iso-Butyric Acid	152	151	153	158	155
	$n=6$	7	8	9	10
Valerianic Acid	163	165	167	154	

They conclude that all esters at their boiling points and at the same pressure transpire very nearly equal volumes of vapor, which however because the boiling points are different, do not contain the same number of molecules.

They found η for the corresponding acids considerably smaller than for their esters. They believed that the differences of η are partly too small and partly too irregular to draw any sure conclusion of the dependence of η on the molecular constitution. They point out, however, some differences which seem quite regular.

The esters of acetic, propionic and isobutyric acids show almost always a smaller η than those of formic, normal butyric

1. Wied. Ann., 1881, Bd. 13, p. 1.

and valerianic acids. This difference is especially noticeable in the two butyric acids. The influence of the alcohol radical cannot be seen so clearly. Among the isomeric esters, those of formic, acetic, propionic and isobutyric acids have the greater η with the greater alcohol radical. The isomeric esters of normal butyric and valerianic acids do not follow this rule but have the same friction.

The number of carbon atoms in a molecule also seems to have a certain influence on η . The esters for which $n = 2, 5, 7$ or 8 show a larger η than those with $3, 4$ or 9 carbon atoms. The cause of these differences they were unable to explain.

On calculating the relative molecular volumes they found them only about half those given by Kopp's rule. L. Meyer tried to account for this by advancing the hypothesis that by Kopp's method the empty space is included which is open to the atoms for their motion, while from the coefficient of internal friction only the volume of the gas particles themselves is determined.

Steudel¹ continued the work of L. Meyer and Schumann, using the same apparatus with the second capillary, the first having been broken. He investigated several homologous lines of organic compounds, viz., alcohols up to four atoms of carbon per molecule, and their halogen derivatives, also some substitution products of ethane and methane.

He found the transpiration time increased with the molecular weight. Of isomeric compounds at the boiling points, the normal, *i.e.*, those that boil at the highest temperature transpire the slowest and the tertiary the fastest, with the exception of isopropyl alcohol which transpires noticeably slower than the normal. Unsymmetrical low boiling compounds have a smaller transpiration time than the symmetrical. The only exception he found to the rule that the transpiration time increases with the molecular weight is methyl iodide whose time was 1037 minutes, which is almost the same as 1056 minutes taken by isobutyl iodide.

He points out that the coefficients of friction of each line of homologous compounds are nearly alike or only slightly different. The values for the primary alcohols vary from .000135 to .000143; for three of them they are almost exactly alike. The isopropyl gave a considerably larger figure, also

1. Wied. Ann. 1882, Bd. 16, p. 369.

TABLE OF $\eta \times 10^6$.

Radical	Alcohol	Chloride	Bromide	Iodide
Methyl	135	116*		245
Ethyl	142	105*	183	216
Normal Propyl	142	146	184	210
Isopropyl	162	148	176	201
Normal Butyl	143	149		202
Isobutyl	144	150	179	204
Tertiary Butyl	160	150		

* Calculated from Graham's results.

the tertiary butyl. The chlorides seem to all have the same friction. The greatest differences exist in the iodide column.

He found a considerable difference in η with a change in pressure. With a greater pressure than 10 to 15 cm. of mercury the formula seemed to lose its validity for vapors. This agrees with what L. Meyer had noticed with benzole.

Steudel also gives tables of molecular velocities, mean free paths, combined cross section of molecules and cross-sections of an equal number of molecules. He points out that the cross sections of molecules of isomeric compounds are not the same. For the butyl compounds the areas for the normal substances are the largest, the tertiary the smallest, with the iso compounds between. Propyl and isopropyl alcohol, as also both chlorides show the same relation. On the other hand, isopropyl-bromide has a greater molecular area than the normal compound. In the substitution products of ethane the symmetrical ones have a larger area than the unsymmetrical.

Steudel also calculated the relative molecular volumes from SO_2 according to the method of L. Meyer, with whom he agrees in finding the volumes about one half as large as those calculated according to Kopp's rule. The ratios of molecular volumes of the different substances, however, are almost the same as the ratios of the volumes according to Kopp.

L. Meyer,¹ summing up Steudel's and his own previous results, gives the following:

TABLE OF $\eta \times 10^6$	
Alcohols	$\text{C}_n\text{H}_{2n+2}\text{O} \dots\dots\dots 142$ average
Chlorides	$\text{C}_n\text{H}_{2n+1}\text{Cl} \dots\dots\dots 150$ "
Esters	$\text{C}_n\text{H}_{2n}\text{O}_2 \dots\dots\dots 155$ "
Bromides	$\text{C}_n\text{H}_{2n+1}\text{Br} \dots\dots\dots 182$ "
Iodides	$\text{C}_n\text{H}_{2n+1}\text{I} \dots\dots\dots 210$ "

1. Pogg. Ann., 1882, Vol. 16, p. 394.

Cases in which $n = 1$ and some few unaccountable variations are omitted from the above. When $n = 1$ the variations are great but he could see no law of the influence of molecular constitution on the friction.

On the other hand the influence of the nature of the atom is very clearly seen; friction of iodine > bromine > chlorine.

The molecular volumes do not agree with those L. Meyer¹ calculated from Graham's results. He points out that this one fact seems certain, viz.: the molecules of a tertiary butyl compound are smaller than those of a secondary which are smaller than those of a primary. This is in agreement with the universal view taken of the concatenation of these compounds. Those of the tertiary are grouped around a single atom of carbon, hence are more spherical in shape. Propyl and isopropyl compounds on the other hand do not show the same regularity. The alcohols and iodides deviate in opposite directions, which is unexplained. He further points out that the sphere of action of a liquid molecule increases with the temperature, while that of a gaseous molecule diminishes with rise of temperature.

In 1881 Crookes² published an interesting account of experiments on the viscosity of gases at high exhaustions. His method consisted in observing the logarithmic decrement of a plate of mica enclosed in a glass bulb, the axis of suspension being in the plane of the mica. He found that with air, nitrogen, oxygen and carbon monoxide η diminishes slightly as the pressure falls from 760 to 3 mm., after which it decreases very rapidly. Hydrogen showed no change in η from 760 to 3 mm. pressure. When the pressure was $\frac{1}{2}$ mm. the mean free path of a molecule became comparable with the dimensions of the glass bulb, and the ultra gaseous state of matter, as Crookes names it, was assumed.

Margules³ suggested a new experimental method of finding the internal friction of a fluid or gas. He proposed two coaxial cylinders, one rotating at a constant speed, the other having its turning moment measured directly. He also pointed out that in Coulomb's method the molecules near the rotating plate do not move in circles but in zigzags, the centrifugal

1. Liebig's Ann., 1867, Suppl. Bd. 5, p. 129.

2. Phil. Trans., 1881, Vol. 172, p. 387.

3. Wien. Ber. Mathem. Naturw., 1881, Bd. 83 (2), p. 588.

force carrying them outward from the axis. This action Maxwell had apparently neglected.

Instead of an oscillating system of plates Braun and Kurz¹ employed a sphere, the mathematical theory of which had been worked out by Kirchhoff. They found η for air at room temperature $= 0.000184 \pm .000010$.

Warburg and Babo² investigated the relation between viscosity and density of fluid, especially gaseous substances. They employed the capillary method, and experimented on liquid CO_2 and gaseous CO_2 above the critical temperature, and at pressures between 30 and 120 atmospheres. They found that the viscosity of liquid CO_2 increases with the density, as does also that of gaseous CO_2 at very high pressures. The fact that investigators have shown that the viscosity of a gas is not independent of the pressure, when the latter is either very low or very high, does not destroy the validity of the law for ordinary pressures.

Grossman,³ noticing that the transpiration and oscillation methods are not in perfect agreement in their values of η , undertook to discover the cause of the difference. He chose Coulomb's method for his work as being the simplest. He proposes corrections within certain limits and deduces a formula which he thinks applies accurately within those limits.

Klemencic⁴ in 1881 published a complete mathematical treatment of the damping of the oscillations of a solid body in liquids and gases. He discusses the cases of spheres and cylinders oscillating and swinging in various manners.

In order to help settle the question of why the coefficient of friction of a gas increases with the temperature Koch⁵ undertook the study of the coefficient of friction of mercury vapor and its dependence on the temperature. Stefan's hypothesis of an ether envelope of the molecule has already been mentioned. O. E. Meyer's explanation that at higher temperatures the bonds between the atoms are loosened so that the molecules on collision penetrate further into each other, thus dimin-

1. Carl Rep., 1882, Bd. 18, pp. 569, 665, 697; 1883, Bd. 19, pp. 343, 605.

2. Wied. Ann., 1882, Bd. 17, p. 390.

3. Wied. Ann., 1882, Bd. 16, p. 619.

4. Wien. Ber. Mathem. Naturw., 1881, Bd. 84 (2), p. 146.

Carl's Rep., 1881, Bd. 17, p. 144.

Ann. d. Phys. Beiblätter, 1882, Bd. 6, p. 66.

5. Wied. Ann., 1883, Bd. 19, p. 857.

ishing the distance between their centres and thus their diameters, does not hold in the case of a monatomic gas such as mercury. Koch employed two capillaries, one having a radius = 0.004245 cm. and length = 9.875 cm.; and the other a radius = 0.00593 cm. and length = 19.22 cm.

He found $\eta = 0.000494$ at 0°C. and $\eta = 0.000643$ at 98°C. With a third capillary whose radius = .008238 cm. and length = 18 cm. he found η 4% larger than the above, hence he concludes Poiseuille's law does not hold for a capillary of this size and neglects this result.

Assuming the usual equation $\eta = \eta_0 (1 + \alpha t)^n$ he found the exponent n to be 1.6 for mercury from which it appears that the diameter of a mercury molecule is about proportional to

$\frac{1}{T^{.55}}$ where T = absolute temperature. At 0°C. he found the

molecular volume of mercury to be 12.9 times, and at 300° only 4.39 times that of hydrogen.

In 1884 O. Reynolds¹ read an interesting and suggestive paper on the two manners of motion of water, the steady or direct, and the sinuous or eddying. He experimented on water flowing through glass tubes and made the character of motion visible by means of color bands in the water. In order that motions in tubes of different sizes can be compared, the velocities must be inversely as the tube diameters. The critical velocity at which sinuous motion begins increases with the viscosity of the fluid. If water be flowing in a bent channel in steady streams, the question as to whether it will remain steady or not turns on the variation in the velocity from the inside to the outside of the stream. He enumerates viscosity, converging solid boundaries, curvature with the velocity greatest on the outside as conducive to direct or steady motion, whereas diverging solid boundaries and curvature with the velocity greatest on the inside, tend to sinuous or unsteady flow. It is possible that similar actions take place in the flow of a gas through a capillary, and constitute an objection to a coiled capillary.

Hoffmann² worked with gases along somewhat the same lines that Reynolds did with liquids. Poiseuille's law takes

1. Proc. Roy. Inst. Grt. Brit., 1884, Vol. 11, p. 44.

2. Wied. Ann., 1884, Bd. 21, p. 470.

for granted that the particles of gas move through a capillary in parallel lines. Hoffmann tried to prove that when this law does not apply it is because the molecules have a sinuous motion through the capillary. He thought that the disturbing cause resides chiefly at the beginning and end of the capillary, although Guthrie's results seemed to contradict this. Hoffmann repeated Guthrie's experiments and found a longer transpiration time for the many small pieces than when the capillary was all in one piece. He points out that perhaps Guthrie worked with too low pressures and put the pieces of capillary too close together.

In order to study the whirling motion he drove tobacco smoke through tubes (of course not capillary) and found a conical contraction of flow at the end, and further on a conical spreading out in which could be seen powerful eddies. The eddies approached nearer to the end as the velocity was increased, until finally the contraction vanished and the eddies were right at the end of the tube. These observations agree with those of Sondhaus.¹ As a result of all his work Hoffmann concludes that when Poiseuille's law does not hold for a tube, the chief reason is the phenomena at the end and especially at the beginning of the capillary.

As it was impossible to determine by the method employed in 1881 by L. Meyer and Schumann, the dependence of the friction of vapors on the temperature, Schumann² proceeded to make this investigation by the oscillation method. His apparatus was similar to Maxwell's, but he found that Maxwell's formula did not give concordant results, so he adopted an empirical formula which gave values in good agreement, but generally smaller than those of other observers excepting Obermayer. His η for air at 20° C. = .000178 and at 0° C. .000168. His results are in fair accord with those of the transpiration method at ordinary temperatures. At high temperatures he claims that capillaries give values which are too small due to the adsorption of the gas by the capillary walls.

To express the increase of η with rise of temperature he proposes a new formula:

$$\eta = \eta_0 \sqrt{1 + \alpha t} (1 + \gamma t)^2$$

1. Pogg. Ann., 1852, Bd. 85, pp. 58.

2. Ann. d. Phys., 1884, Bd. 23, p. 353.

in which α = coefficient of expansion of the gas, and γ = coefficient of diminution of the radius of the sphere of action of the molecule. For air $\alpha = 0.003665$, $\gamma = 0.000802$. For CO_2 $\alpha = 0.003701$, $\gamma = 0.000889$. For all vapors α is .004, but for benzole $\gamma = 0.00185$ while for other vapors it is 0.00164.

He found η entirely independent of the pressure except when the vapor was saturated.

On calculating the molecular volumes he found them to be from 44 to 72% of the values calculated according to Kopp's rule.

Schneebeli¹ in 1885 attempted to get with the greatest accuracy the absolute value of the coefficient of friction of air and its dependence on the temperature. He used five different capillaries and obtained the following values of $\eta \times 10^7$ at 0° C.: 1712, 1690, 1698, 1703, 1734, corrected for the vapor tension of water. For its variation with the temperature he proposed the formula $\eta_t = \eta_0 (1 + 0.0027 t)$. His values agree quite well with those which Obermayer obtained ten years before.

Koenig² studied the influence of magnetization and electrification on the coefficient of friction and could detect none. He made an important contribution to the subject of internal friction by deducing a correction for Coulomb's method which brought its results down into agreement with those of the capillary method.

Tomlinson³ made a very careful study of the coefficient of viscosity of air and its change with the temperature. He observed the logarithmic decrement of the torsional vibrations of cylinders and spheres. He found η at 0° C. = .00017155 and thought Holman's formula correct, $\eta_t = \eta_0 (1 + 0.002751 t - 0.00000034 t^2)$. This result is about 9% lower than Maxwell's, which Stokes explains on the supposition that Maxwell's disks were not exactly level. Tomlinson also studied the effect of aqueous vapor in the air. He says that air at 15° C. and 760 mm. pressure when saturated with aqueous vapor is only .2% more viscous than dry air. It is only when under a pressure less than 350 mm. that the aqueous vapor begins to show an appreciable effect; but when the rarefaction is great, moist air becomes considerably *less* viscous than dry air. Crookes had

1. Archiv. de Genève, 1885, Vol. 14 (3), p. 197.

2. Wied. Ann., 1885, Bd. 25, p. 618; 1887, Bd. 32, p. 193.

3. Phil. Trans., 1886, Vol. 177 (2), p. 767.

likewise said that at 15° C. and pressures 760 to 350 mm. the presence of aqueous vapor has little or no effect on the internal friction of air.

Lampel,¹ after reviewing the mathematical treatment of the torsional oscillations of a sphere with air resistance given by Lampe,² Boltzmann⁴, Kirchhoff and Klemencic, proceeded to determine which of these men came nearest the truth. His experiments showed that Boltzmann's formula is the best.

In 1887 O. E. Meyer³ revised his mathematical treatment of Coulomb's method, accepting the correction which Koenig had been fortunate enough to devise for the disturbance which takes place at the edges of the cylindrical surface of the disks. He showed how this correction improved his previous values for η .

Because the French physicist, Hirn, rejected the kinetic theory of gases for the reason that he could find no increase in the coefficient of friction of air with increase of temperature De Heen⁵ undertook an investigation of this subject. His method consisted in letting a brass piston descend under gravity in a tube and drive air through a capillary stopcock at the bottom. His pressures varied from 10 to 2280 mm. of mercury. He found η at low pressures smaller and at high pressures larger than at ordinary pressures. He maintains that below 80 mm. pressure η varies as the square root of the absolute temperature in accordance with the kinetic theory of gases. After passing 80 mm. pressure η increases more rapidly with the temperature than at lower pressures, the variability of η attaining a maximum at 300° C. He thinks that the disagreement between theory and experiment may be due to the fact that the mean free path of a molecule is possibly not a straight line in gases which are under the relatively high pressure of the atmosphere.

Couette⁶, criticizing Coulomb's method as giving only an ap-

1. Wien. Ber., 1886, Bd. 93 (2), p. 291.

2. Programm des Städt. Gym. zu Danzig, 1866.

3. Ann. d. Phys., 1887, Bd. 32, p. 642.

Sitz. d. Münch. Akad., 1887, Bd. 17, p. 343.

4. Wien. Ber., 1881, Bd. 84 (2), p. 40.

5. Bull. de l'Acad. de Belgique, 1888 (3), Vol. 16, p. 195.

6. Comp. Rend., 1888, Vol. 107, p. 388.

Jour. de Phys., 1890 (2), Vol. 9, p. 414.

Ann. de Chim. et de Phys., 1890 (6), Vol. 21, p. 433.

proximation, even with very slow oscillations, and Poiseuille's method, as being true only for very slow rates of flow, adopted the method suggested by Margules in 1881. He used two copper cylinders, the inner suspended by a torsion thread and the other one coaxial with it, revolving with a constant velocity. The outer cylinder tends to set the inner one in motion, which is kept in its primitive position by turning the torsion head through a measured angle. He found the angle of torsion divided by the revolutions per minute to be almost constant, increasing only very slightly with the speed. His value of η for air at 18° C. = .0001847.

Barus¹ made a careful investigation of the viscosity of gases at high temperatures. His capillary was of platinum, radius at 0° C. = 0.0079, coiled into a helix. The range of temperature was from 5° to 1400° C.

He found that the *mean* increase of gaseous viscosity was proportional to the $\frac{3}{4}$ power of the absolute temperature and not in accordance with Schumann's or Holman's formula. He suggested that if the law connecting η and the temperature were rigorously known his apparatus could be used as a pyrometer. He pointed out that below 100° air is not rigorously a perfect gas, because below that temperature its temperature exponent increases to 0.73. Above 100° C. it is 0.67 the same as for hydrogen whose exponent does not change from 0° to 1400° C. Obermayer showed that as the state of vapor is approached the temperature exponent increases, being nearly 1 for many vapors. Barus's absolute values of η are not good, that for air at 0° C. being 0.0002472 to 0.0002508, which is much too high.

Sutherland² showed that the discrepancy between theory and experimental results concerning the increase of η with the temperature, disappears if, in the theory account is taken of the forces of attraction between molecules when the latter approach each other. These attractive or cohesive forces tend to increase the number of collisions between the molecules, and thus have the effect of apparently increasing the diameter

-
1. Amer. Journ. Sci., 1888 (3), Vol. 35, p. 407.
Bull. of U. S. Geol. Survey, No. 54, Washington, 1889, p. 239.
Wied. Ann., 1889, Bd. 36, p. 358.
Phil. Mag., 1890, Vol. 29, p. 337.
 2. Phil. Mag., 1893 (5), Vol. 36, p. 507.

of the sphere of action. With increased molecular velocity, due to rise of temperature, the cohesive forces have less chance to act than at lower molecular velocity. *i.e.*, at lower temperature. Therefore the sphere of action will be increased less at high than at low temperatures, which produces the same result as if it diminished at higher temperatures. Sutherland proposed the following formula which agrees well with the observations of Holman and Barus:

$$\eta = \eta_0 \left(\frac{T}{273} \right)^{\frac{1}{2}} \frac{1 + \frac{C}{273}}{1 + \frac{C}{T}}$$

in which T is the absolute temperature, and C is the cohesion constant depending upon the nature of the gas, which for air = 113.

Ortloff¹ made a careful study of the friction of the three gases C_2H_6 , C_2H_4 and C_2H_2 by the transpiration method. He found that the difference in cross section of the molecules C_2H_6 and C_2H_4 is less than that between C_2H_4 and C_2H_2 , the relative values being 342, 298 and 228. O. E. Meyer² claims that the cross section of a molecule = sum of the cross sections of its atoms. Ortloff found that his molecular cross section was less, his molecular diameter less, and his molecular volume greater than those calculated according to Meyer, with the exception of the C_2H_2 volume. He concludes that his gas atoms cannot be disposed in a plane. Meyer's supposition that the molecular volume = sum of the atomic volumes presupposes that the atoms are grouped in a sphere. Ortloff's experiments seemed to show that of his three gases this is true only in the case of C_2H_2 .

Noyes and Goodwin³ investigated the viscosity of the vapor of mercury because the latter is a monatomic element. They used the transpiration method and experimented also on hydrogen and carbon dioxide. They found that the cross section of a mercury molecule is 2.48 times as large as that

1. Inaug. Diss. Jena, 1895.

2. Kinetic Theory of Gases, 1899, Chapter X.

3. Physical Review, 1896, Vol. 4, p. 207.

Zeitsch. Physik. Chem., 1896, Vol. 21, pp. 671-679.

of hydrogen at 300° C. They concluded that atoms and molecules are of the same order of magnitude, and that the spaces between the atoms within the molecule, if any exist, are not large in comparison with those occupied by the atoms themselves, and that therefore the coefficient of friction is not adapted for distinguishing between monatomic and polyatomic molecules. They believed that this explains the fact that the molecular cross section of most comparatively simple molecules is approximately equal to the sum of the atomic cross section as had been pointed out by O. E. Meyer. Their work is open to criticism because a joint in their apparatus could not be made air tight.

Houdaille¹ measured the coefficient of friction of air and vapor of water by the transpiration method. At 76 cm. pressure he found $\eta_0 = 0.000186$ for air, and for water vapor = 0.0000975. At a pressure of between 1 and 3 cm. he found η_0 for air the same, while η_0 for water vapor changed to 0.0000885. He found fair agreement between the calculated and observed values of the diffusion coefficient for water vapor.

Pérot and Fabry² brought out a new kind of absolute electrometer intended for the measurement of small differences of potential. They observed that it attained its position of equilibrium very slowly when the distance between the plates was small, owing to the viscosity of the layer of air which separates them. Thus they obtained a new method for determining the viscosity of air, which they found to be 0.000173 at 13° C.

Jaeger³ gave a careful mathematical analysis of the influence of molecular volume on the internal friction of gases taking account of association and expansion of molecules. Instead of the usual formula $\eta = \frac{1}{3} d G L$ he proposed $\eta = \frac{5}{12} d G L$ in which d = density, G = velocity of mean square, L = mean free path of a molecule. He also gave the formula $\eta = \eta_0 \frac{(1 + 4 \beta A)^2}{A}$ in which $A = 1 + \frac{5}{2} \beta +$ and $\beta = \frac{b}{v}$ = ratio of the molecular and specific volumes.

1. Fortschr. d. Phys., 1896, 52, Jahr. I., p. 442.

2. Compt. Rend., 1897, Vol. 124, p. 28.

Ann. de Chim. et de Phys., 1898 (7), Vol. 13, p. 275.

3. Wien. Ber. Mathem. Naturw., 1899 (2), Vol. 108, p. 447.

“ “ “ “ 1900 (2), Vol. 109, p. 74.

Breitenbach,¹ using the transpiration method, experimentally determined the coefficients of friction of air, ethylene, carbon dioxide, methyl chloride, and hydrogen. He found that η varies according to a power of the absolute temperature whose exponent for different gases varies between 0.6 and 1.0. He inferred that the sphere of action of a molecule diminishes with increase of temperature. For the same gas this exponent decreases with increasing temperature. Also a lowering with lower temperatures was noticed. In gaseous mixtures η does not vary as the composition, and Puluj's formula is only approximately correct. The difference between the results of the oscillation and transpiration methods at high temperatures cannot be explained by an increase of the slipping of the gas along the capillary walls. This slipping he found could in general be neglected.

Two years later Breitenbach² compared his work with Sutherland's formula for the variation of η with the temperature, and found this formula gave very excellent agreement with his experiments. The value of the cohesion constant for air he found to be 119.4 instead of 113 according to Sutherland.

Rayleigh³ on the supposition that $\eta_t = \eta_0 (1 + \alpha t)^n$ found the exponent n for dry air = 0.754, for oxygen = 0.782, for hydrogen 0.681, for argon (impure) 0.801, for pure argon = 0.815. Later, using Sutherland's formula, he found the cohesion constant to be the same for hydrogen and helium, viz.: 72.2, and this value and those for air, oxygen and argon agree well with the values calculated by Sutherland from Obermayer's observations.

Schultze⁴, like Rayleigh, used the transpiration method for investigating the internal friction of argon and its change with the temperature. He found its friction at 0° C. to be 2104×10^{-7} and that it varied with the temperature in accordance with Sutherland's formula, the cohesion constant being 169.9. His argon contained $\frac{1}{2}\%$ of nitrogen.

Job⁵ called attention to a new method of measuring the resistance offered by a capillary tube to the flow of gases. A voltmeter is provided with a capillary outlet; the pressure

1. Wied. Ann., 1899, Bd. 67, p. 803.

2. Drude's Ann., 1901, Bd. 5, p. 166.

3. Proc. Roy. Soc., 1900, Vol. 66, p. 68; Vol. 67, p. 137.

4. Drude's Ann., 1901, Bd. 5, p. 140.

5. Bull. Soc. Franc. Phys., 1901, Vol. 157, p. 2.

produced in the voltameter for a given current, measures the resistance of the capillary. The author suggests the application of this method to various experiments in connection with the flow of gases.

F. G. Reynolds,¹ using spheres and cylinders in torsional oscillation, determined the viscosity coefficient of air, and investigated the effect upon it of Röntgen rays. His value of η at $21^\circ \text{C.} = 187 \times 10^{-6}$. The results of his experiments with Röntgen rays seem to show that their effect is scarcely, if at all perceptible.

Bestelmeyer,² using transpiration apparatus very similar to Holman's, investigated the change in the coefficient of internal friction of nitrogen for a temperature range of -192°C. to $+300^\circ \text{C.}$ and found that Sutherland's formula applied with satisfactory accuracy except at -192° where it was 2% in error, perhaps owing to change in the law at this low temperature. The cohesion constant was found to be 110.6.

Markowski,³ employing the same transpiration apparatus used by Schultze in 1901, studied the internal frictions of oxygen, hydrogen, chemical and atmospheric nitrogen, and their change with the temperature. He corrected all his results for slip, using coefficients of slip determined by Breitenbach Kundt and Warburg, for air, oxygen and hydrogen. For nitrogen he used the molecular free path, which is theoretically nearly equal to the coefficient of slip.⁴ His corrected value of η for air at $15.9^\circ \text{C.} = 1814 \times 10^{-7}$, and at $99.62^\circ = 2212 \times 10^{-7}$. The correction for slip amounted to $\frac{1}{2}\%$. He states that Graham's results are preferable to those of Obermayer. Sutherland's formula he found to give excellent results from 0° to 183°C. He also tried the older exponential formula and found the exponent diminishes with rise of temperature as had been noticed by several other observers. Pulum's formula for the friction of a gaseous mixture he found applies well to atmospheric nitrogen as a mixture of chemically pure nitrogen and argon.

Kleint,⁵ continuing the work of Schultze and Markowski

1. Phys. Review, 1904, Vol. 18, p. 419; Vol. 19, p. 37.

2. Inaug. Diss. Munich, 1902.

Ann. d. Phys., 1904, Bd. 13, p. 944.

3. Inaug. Diss. Halle, 1903.

Ann. d. Phys., 1904, Vol. 14, p. 742.

4. O. E. Meyer's Kinetic Theory of Gases, 1899, p. 211.

5. Inaug. Diss. Halle, 1904.

with the same piece of apparatus investigated the friction of mixtures of oxygen, hydrogen and nitrogen. He found Pulu's formula to give only approximately the coefficient of friction of a mixture of gases. He observed that small percentages of oxygen and nitrogen raise the friction of hydrogen markedly, while hydrogen only begins to make itself felt upon the others when it is 5% of the mixture. Sutherland's formula for the increase of η with the temperature he found to be correct.

METHOD EMPLOYED IN EXPERIMENTAL INVESTIGATION.

The preceding historical review shows that the methods employed in the past for determining the coefficient of the internal friction of gases, may be divided into two general classes: those in which the movement of a solid body in the gas is observed, and those in which the time of passage of the gas through a capillary tube is noted. There are many modifications of both general methods, especially of the first named one which is the earlier historically. Owing to the difficulty of getting capillaries of perfectly uniform bore, and of determining with the greatest accuracy the shape and size of their cross section, and also owing to the possible formation of eddies at the beginning and end of the flow, and to the possible slipping of the gas on the capillary walls, probably the oscillation method is the better for absolute measurements, provided a solid body is employed of such a shape that the mathematical treatment is rigorously correct. It seems certain however that the transpiration method has been growing in favor of late years, and that it is more convenient for comparative measurements than the other method. As already stated my object was more to get comparative than absolute values of the greatest accuracy, hence the transpiration method was decided upon for this experimental investigation.

GENERAL DESCRIPTION OF APPARATUS.

The form of apparatus and the subject of this research were kindly suggested to me by Professor Morris Loeb, under whose guidance these experiments have been made. The apparatus consists essentially of a U shaped tube (see Fig. 1), one limb of which is capillary, while the other is not, but serves as a cylinder of known capacity, down which is forced by gravity a piston consisting of a column of mercury, which drives the gas under it up through the capillary limb. The capillary, A,

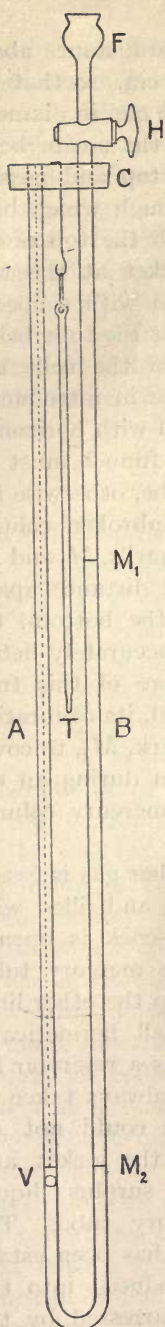


FIG. 1.
View perpendicular to the
plane of the two limbs.

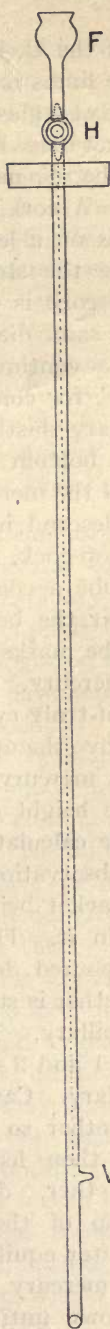


FIG. 2.
View in the plane of
the limbs.

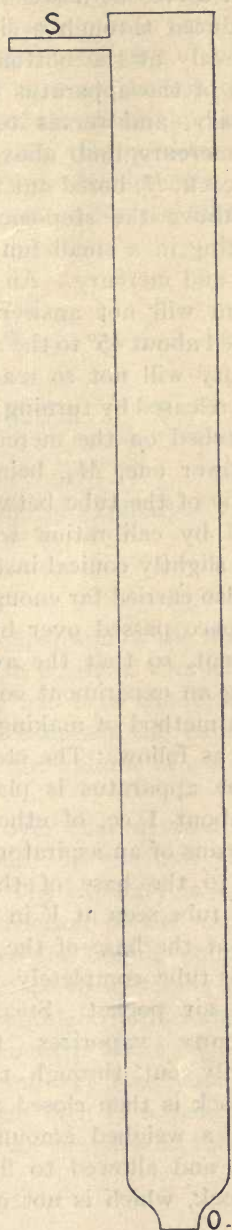


FIG. 3.
Steam Jacket.

does not begin at the bend of the U, but some distance above it. The distance between the limbs is only 3 cm., so that the apparatus can be placed inside of a glass tube 5 cm. in diameter which serves as a steam jacket (see Fig. 3), the steam being introduced through a side tube, *S*, near the top and passing out freely at the bottom, *O*. A cork, *C*, through which both limbs of the apparatus pass is on a level with the top of the capillary, and serves to close the steam jacket at the top. The mercury limb above the cork is provided with a special stop-cock, *H*, bored out to the same diameter as the tube below it. Above the stop-cock is a continuation of the tube terminating in a small funnel, *F*, for convenience in introducing ether and mercury. An ordinary thistle funnel with horizontal bottom will not answer; the bottom of the funnel must be inclined about 45° to the axis of the mercury tube, otherwise the mercury will not so readily descend in one unbroken column when released by turning the stop-cock. Two marks, M_1 and M_2 , are etched on the mercury tube a convenient distance apart, the lower one, M_2 , being near the bend at the bottom, the volume of the tube between the marks being accurately determined by calibration with mercury. The bore of this tube being slightly conical instead of truly cylindrical, its calibration was also carried far enough above the upper mark, M_1 , to cover the space passed over by the mercury column during an experiment, so that the average height of the mercury column during an experiment could be calculated.

The method of making an observation on ether gas is essentially as follows: The steam jacket being cold and filled with air the apparatus is placed in it. The stop-cock is opened and about 1 cc. of ether is poured down the mercury tube. By means of an aspirator the ether is sucked up the other limb close to the base of the capillary. The small hermetically closed tube seen at *V* in Figs. 1 and 2 serves as a reservoir for ether at the base of the capillary. Care was always taken to fill this tube completely with ether so that it could not act as an air pocket. Steam is then led into the jacket and of course vaporizes the ether, driving surplus liquid violently out through the top of the mercury tube. The stop-cock is then closed and after equilibrium has been established, a weighed amount of mercury is introduced into the funnel and allowed to flow down until it is arrested by the stop-cock, which is not quite air tight, because no grease can

be used in it for fear of soiling the mercury. The stop-cock is then suddenly turned and the mercury descends in a solid column. When its lower meniscus passes the upper mark on the tube a stop watch is started, which is stopped as the same meniscus passes the lower mark. The barometer is read when the mercury has covered half the measured distance. A thermometer, *T*, Fig. 1, hanging from the cork at the top of the steam jacket indicates the temperature of the steam, and serves as a plumb line. The readings of this thermometer were corrected by comparison with a standard thermometer. The coefficient of friction of the gas is calculated by the following formula given by O. E. Meyer:¹

$$\eta = \frac{\pi g d r^4}{16 L V} \frac{P^2 - p^2}{P} t$$

in which *d* = density of mercury at 0° C

g = acceleration due to gravitation

r = radius of capillary in cm.

L = length of capillary in cm.

P = pressure of gas on entering the capillary.

p = height of barometer at 0° C

t = time in seconds

V = c.c. of gas transpired.

No allowance need be made for the expansion of the mercury at 100° C., for what the column gains in height is compensated for by loss in density. No allowance has been made for the expansion of the capillary as it was assumed the expansion of the mercury tube, hence increase of the volume of gas transpired, would counteract this.

The advantages of this apparatus over that devised by L. Meyer are quite obvious and numerous. In the first place it is much more simple and available. The capillary is straight instead of coiled into a helix. The friction of the vapors is taken at a temperature so high above the boiling point that they behave more like true gases than at their boiling points, where they are in a condition of unstable equilibrium. The length of time required for an experiment is short enough for all conditions to be kept constant, and yet long enough, so that with a stop watch reading to one fifth of a second, the time can be determined to within less than one part in a thousand.

1. Pogg. Ann., 1866, Bd. 127, p. 269.

APPARATUS NO. 1.

The first piece of apparatus was constructed more to test the practicability of the method than for getting accurate results. It having been determined by experiment, that the largest diameter of tube in which a mercury column would hold together, against a cushion of air, was about .35 cm., this apparatus was constructed with a mercury tube whose mean diameter, where it was traversed by the mercury column was .35104 cm., as shown by the fact that 76.0405 grams of mercury occupied 58.05 cm. at 20° C. The distance between the two etched marks on the tube was 50 cm. This distance was occupied by 65.5558 grams of mercury at 20° C. The density of mercury at this temperature being 13.5463 the volume between the two marks was 4.8394 cubic centimetres.

The capillary was 34.35 cm. in length which was only about half the length of the mercury tube forming the other side of the U, in other words the capillary formed the upper half of one side of the U. Its bore was conical as shown by the fact that 9.50 cm. of mercury at the small end occupied 9.05 cm. at the larger end which was made the bottom because O. Reynolds¹ has shown that converging walls tend to a steady instead of a whirling flow of water and presumably also of gas. The above column of mercury was passed slowly from one end of the capillary to the other and changed its length gradually and steadily, thus showing the absence of abnormal contractions or expansions of the bore. The bore of the capillary was determined from a sample 5.75 cm. long which had been cut from the smaller end. This sample was weighed several times empty and when containing different columns of mercury and the radius of the bore determined in the well known way. A section was also examined under a microscope with a micrometer eye piece, and found to be so nearly a true circle that it was taken for such. The microscope reading agreed well with the mercury determinations of the radius. After taking the average of the mercury and microscope readings and after allowing for the taper of the capillary its mean radius was found to be .0103908 cm.

To facilitate the washing of the apparatus the small vent, V, in Figs. 1 and 2, was left about $\frac{1}{2}$ cm. below the base of the capillary. This vent tube which was only 1 cm. long was

1. Proc. Royal Inst. Grt. Brit., 1884, Vol. 11, p. 44.

hermetically sealed off after the apparatus was washed and ready for use. The apparatus, after it was received from the glass blower, was washed throughout with a solution of potassium permanganate made alkaline with caustic potash, then with a solution of the same substance made acid with dilute sulphuric acid. Later a half and half solution of potassium bichromate and strong sulphuric acid was substituted for the above. Sometimes also strong nitric acid, followed by dilute nitric acid was used. Then followed many washings with distilled water. The apparatus was then dried, by sucking through it by means of an aspirator, hot air which was filtered through cotton and dried by calcium chloride. A column of calcium chloride was also placed in the connection between the aspirator and the apparatus. The drying was not hastened by the use of alcohol or ether. The mercury was cleansed by shaking with dilute nitric acid, passing through a fine pin hole and drying in a porcelain dish at 110°C .

TABLE OF THE INTERNAL FRICTION OF AIR.

Temp. in $^{\circ}\text{C}$	Ht. of driving Col. in cm.	APPARATUS No. 1.				Average $\eta \times 10^7$
		Barom. at 0°C	Press. of entering Gas	Time in seconds	$\eta \times 10^7$	
15	7.97	76.03	83.09	76.04	1872	1863.8 ± 2.57
14.9	7.97	76.03	83.09	75.0	1862	
14.9	7.97	76.03	83.09	74.8	1857	
14.9	7.966	76.03	83.09	75.2	1866	
14.9	7.966	76.60	83.64	75.2	1860	
15.4	7.966	76.60	83.64	75.4	1865	
20.4	4.29	75.38	78.87	156.8	1967	1972 ± 3.5
20.2	4.29	75.38	78.87	157.6	1977	
21.4	9.48	75.38	84.01	64.4	1935	1932 ± 2.0
21.4	9.48	75.38	84.01	64.2	1929	
99.9	9.48	75.38	84.01	75.6	2272.5	2296.5 ± 15.8
99.9	9.48	75.38	84.01	76.0	2284.5	
100.3	7.98	76.96	84.00	92.0	2238.2	
100.3	7.98	76.96	84.00	89.8	2185.0	
100.3	7.97	76.60	83.64	94.0	2305.0	
100.3	7.97	76.60	83.64	96.4	2384.5	
100.3	7.97	76.60	83.64	92.7	2293.0	
100.3	7.97	76.60	83.64	94.0	2325.0	

The results of experiments on air with this apparatus are given in the preceding table. It will be noticed they are all rather high, but prove at any rate that the method and apparatus are practicable. The probable errors were calculated by the usual formula $0.6745 \sqrt{\frac{\sum \text{diff}^2}{n(n-1)}}$. The error for readings at 100° C.

is large, probably owing to an error of the stop watch, whose hand showed a tendency to fly forward when stopping near 90 seconds. In one case the hand flew forward 10 seconds. The watch was of course repaired as soon as this defect was noticed. In those cases where the mercury was allowed to run back and was used over again the readings were weighted less than independent readings, three readings being converted into two by taking their means, and four into three in the same way.

It is rather difficult to tell what is the true coefficient of the internal friction of air. Landolt and Boernstein¹ give η for air at 15° C. 1784×10^7 . Markowski² at 16° gives 1814×10^7 , Kleint³ at 14.1 to 14.5° C. gives 1808×10^7 . According to Landolt and Boernstein then, my readings are $4\frac{1}{2}\%$ too high at 15°, while according to Markowski & Kleint they are about 3% too high. F. G. Reynolds⁴ gives for air at 20.7° .000187 which is $3\frac{1}{4}\%$ lower than my result of .0001932 at 21.4° C.

It was found by repeated trials with di-ethyl ether, that the surface tension of the mercury was so much reduced by contact with the ether gas, that the mercury would not hold together in one column in apparatus No. 1. It was determined by experiment that the mercury piston could not be used for ether gas in a tube whose diameter was much larger than 2 mm. A second piece of apparatus was accordingly constructed with a mercury tube of about this size, and a finer capillary, so that the transpiration time would be increased and greater accuracy be secured.

APPARATUS No. 2.

The capillary selected for this when examined with a simple microscope was at first thought to be circular in cross section,

-
1. Phys. Chem. Tabellen, Landolt & Boernstein, 1893.
 2. Inaug. Diss. Halle, 1903.
 3. Inaug. Diss. Halle, 1904.
 4. Physical Rev., 1904, Vol. 18, p. 419; Vol. 19, p. 37.

but the use of a high power microscope with micrometer eye piece showed it to be very elliptical, the ratio of the axes being almost exactly as 3 is to 1. The area of its cross section was determined by mercury several times and these values averaged with the microscope reading with which they agreed well.

The capillary which was 84 cm. long tapered in its bore, 2.5 cm. of mercury at the large end becoming 2.685 cm. at the small end. The sample whose bore was determined was taken from the small end. After allowing for the taper of the bore the average semi-major axis was found to be .006057 cm. and the average semi-minor axis .002016 cm. The capillary was placed with its larger end downward and reached to within 15 cm. of the bend in the U.

The mean diameter of the mercury tube in that part traversed by the mercury piston during an experiment was .2012 cm. as shown by the fact that 31.3 grams of mercury occupied a length of 72.6 cm. at 16° C. The marks on the mercury tube were made 50 cm. apart, the volume between these marks being found by means of mercury to be 1.5707 c.c.

Because the capillary was elliptical the formula used for calculating the internal friction of gas from this apparatus is

$$n = \frac{\pi d g}{8 L V} \frac{a^3 b^3}{a^2 + b^2} \frac{P^2 - p^2}{P} t$$

where a = semi major axis of ellipse of capillary

b = semi minor axis of ellipse of capillary

d = density of mercury at 0° C

g = acceleration due to gravitation

L = length of capillary

V = vol. of gas transpired

P = pressure of entering gas

p = pressure of leaving gas = barom. at 0° C.

t = time in seconds.

The results with air with this apparatus are shown in the next table.

It will be noticed that the values of η are somewhat lower than for apparatus No. 1, and therefore nearer the correct values.

The different lengths of the capillary given in the first column are due to the fact that on several occasions the upper end of

the capillary became stopped with dust from the atmosphere and had to be cut off. When not in use the capillaries were kept capped with rubber, the funnels filled with cotton and closed by corks in which were inserted tubes of chloride of calcium.

TABLE OF THE INTERNAL FRICTION OF AIR.

APPARATUS No. 2.

Length of cap.	Temp. in C°	Ht. of driving Col.	Barom. at 0° C	Pres. of Gas entering	Time in seconds	$\eta \times 10^7$	Average $\eta \times 10^7$
81.8	12.5	23.17	75.74	97.92	2604	1864.2	
84.	18.5	23.17	76.19	98.36	2721.	1897.4	
84.	19.9	23.15	76.26	98.41	2715.	1892.0	1897.3 \pm 3.5
84.	19.9	23.42	76.41	98.82	2700.	1902.5	
84.	20.9	23.15	76.26	98.41	2730.	1902.2	
84.	26.9	23.16	76.15	98.31	2810.	1957.1	
84.	29.1	23.17	75.90	98.08	2830.	1973.6	
84.	100.	23.17	75.91	98.09	3201.	2233.0	2242 \pm 5
81.8	99.9	23.14	75.70	98.85	3130.	2237.0	
81.8	100.2	23.14	76.51	98.65	3155.	2257.0	

TABLE OF THE INTERNAL FRICTION OF AIR.

APPARATUS No. 3.

73.25	10.	18.746	76.78	94.56	509.8	1843.8	
73.25	13.3	18.75	76.78	94.56	516.	1866.9	
73.25	14.4	18.74	76.80	94.58	518.2	1870.0	
73.25	19.4	18.75	76.00	93.79	524.6	1894.0	
73.25	20.8	18.74	75.99	93.78	531.2	1917.2	1909.9 \pm 7.2
70.	21.0	18.75	76.99	94.77	509.2	1923.6	
70.	20.8	18.75	76.95	94.74	500.0	1889.0	
70.	100.	18.74	75.76	94.50	592.8	2244.0	2246.3 \pm 7.2
70.	100.1	18.74	76.19	94.93	599.	2267.0	
70.	100.3	18.75	77.13	94.92	588.8	2228.0	

PREPARATION OF ETHERS.

The di-ethyl ether used in the following experiments was sulphuric ether, U. S. P. purified by two washings with concentrated sulphuric acid, C. P., each of these washings being followed by one with distilled water. It was then shaken with mercury and dried with sodium wire from which it was distilled into glass tubes which were afterward hermetically sealed.

TABLE OF INTERNAL FRICTION OF ETHER GASES.

APPARATUS No. 2.

Length of Capillary	Kind of Gas.	Temp. of Gas	Ht. of driving Col. at 0° C	Barom. at 0° C	Press. of entering Gas	Time in seconds	$\eta + 10^7$	Average $\eta + 10^7$
81.8	Methyl-	99.9	23.16	75.68	97.85	1502.0	1074.5	1092.3 \pm 6.4
81.8	Ethyl	100.	23.20	76.09	98.30	1537.8	1103.	
81.8	Ether	99.9	23.19	75.87	98.07	1471.0	1053.9	
81.8		99.9	23.16	75.44	97.61	1558.0	1114.2	
81.8		100.	23.06	76.28	98.35	1550.2	1105.4	
81.8		100.	23.16	76.15	98.32	1540.0	1102.8	
84.	Methyl-	100.	23.90	76.28	99.18	1380.0	990.9	1004.3 \pm 5.5
84.	Propyl	100.	23.22	76.23	98.46	1409.6	985.4	
84.	Ether	100.	23.28	76.18	98.47	1402.2	982.5	
84.		100.1	23.14	76.46	98.60	1461.8	1018.9	
82.5		99.9	23.13	75.31	97.46	1440.4	1021.2	
81.8		99.8	23.11	74.24	96.39	1439.0	1027.0	
81.8	Methyl-	100.3	23.15	77.15	99.30	1481.4	1061.1	1054.8 \pm 5.0
81.8	Isopro-	100.3	23.14	77.10	99.24	1526.0	1081.1	
81.8	pyl	100.	23.13	76.01	98.24	1459.6	1047.3	
81.8	Ether	100.	23.12	76.00	98.13	1455.0	1039.9	
81.8		100.	23.14	76.00	98.15	1460.8	1044.9	999. \pm 3.3
84.	Di-Eth-	100.1	23.42	76.39	98.81	1410.0	993.4	
84.	yl Eth-	100.	23.42	76.08	98.51	1404.0	990.6	
84.	er	100.	23.16	76.15	98.32	1416.6	986.8	
84.		100.	23.17	76.10	98.28	1417.6	988.6	
84.		100.1	23.16	76.54	98.71	1437.6	1000.6	
82.5		99.9	23.16	75.71	97.89	1434.6	1017.8	
82.5		99.9	23.21	75.50	97.73	1428.0	1015.2	
84.	Ethyl-	100.	23.17	76.06	98.24	1285.0	896.2	915.2 \pm 5.3
84.	Propyl	100.	23.17	75.89	98.07	1296.4	904.6	
84.	Ether	99.9	23.16	75.70	97.87	1281.2	892.7	
81.5		99.9	23.15	75.58	97.75	1295.8	930.5	
81.5		99.9	23.14	75.57	97.73	1298.8	932.3	
81.5		99.9	23.15	75.57	97.74	1300.8	934.0	

The ethyl-propyl ether, methyl-propyl ether and methyl-ethyl ether used in this investigation were prepared by me in the research laboratory of New York University under the personal supervision of Professor Loeb, according to the continuous etherification method described by Norton and Prescott in the *Am. Chem. Journal*, 1884, Vol. VI., p. 241. They were carefully dried with sodium and kept in sealed tubes.

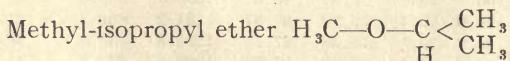
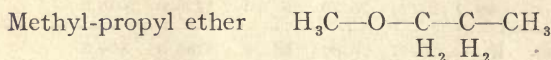
The other substances, viz.: di-methyl ether, ethyl alcohol, methyl-isopropyl ether, ethyl-isopropyl ether, di-propyl ether, isopropyl-propyl ether and di-isopropyl, I owe entirely to the great courtesy of Professor Loeb, as I had no part at all in their preparation. As far as is known this is the first time that

methyl-isopropyl ether has ever been made, while ethyl-isopropyl ether and isopropyl-propyl ether have probably been made only once before.

The internal frictions of the ethers used in apparatus No. 2 are given in the foregoing table on page 43.

The ethers are arranged in this table in the order of their molecular weights; that of methyl-ethyl ether being 60.064, that of methyl-propyl, methyl-isopropyl, and di-ethyl ether being alike 74.08; while that of ethyl propyl is 88.096. It will be noticed the smaller the molecular weight the greater is the internal friction, which agrees well with the kinetic theory of gases, according to which the friction increases with diminished size of molecule.

The most noteworthy fact shown in this table is that the three isomeric ethers, di-ethyl, methyl-propyl and methyl-isopropyl have not the same internal friction. Di-ethyl ether and methyl-propyl practically agree, while methyl-isopropyl ether has a friction 5% higher. According to the universally accepted view of the concatenation of the molecules of these substances, the first two are simple chain compounds, while the last is a chain compound with two branches:



It is easily conceivable how the last arrangement results in a compacter, smaller molecule, and hence shows a higher internal friction.

Although the amount of liquid used varied from $\frac{1}{2}$ cc. to 1 cc. as a rule, this small amount seemed sufficient on vaporizing to drive all the air out of the apparatus, as filling the apparatus entirely with ether from the base of the capillary to the stop-cock did not give results different from those obtained using 1 cc. of ether.

The weight of mercury used in apparatus No. 1 and No. 2 was usually about 10 grams. That in apparatus No. 3 shortly to be described was about 5 grams.

The allowance to be made for the friction of the mercury against the walls of the tube was determined in the following

manner. Three readings with air were taken with three different columns of mercury, under constant temperature conditions. It being known that the internal friction of a gas is independent of the pressure, the values of η from these three readings were equated to each other in pairs, giving, after cancelling out constants of the apparatus, equations of the form

$$\frac{P^2 c^2 - p^2}{P c} t = \frac{P_1^2 c^2 - p_1^2}{P_1 c} t_1$$

in which c is a constant reduction factor due to the friction of the mercury against the walls of the tube. The effect of capillarity is probably negligible, because the upper and lower surfaces of the mercury are convex in opposite directions.

In solving the equations for c good agreement was found, the average c for apparatus No. 1 being .9892. For apparatus No. 2 $c = .9895$ and for apparatus No. 3 $c = .9894$, all at 100°C . The pressure of the gas on entering the capillary was calculated by adding the height of the mercury column at 0°C . to the barometer at 0°C . and multiplying by the reduction factor given above. The mercury and barometer column were reduced to 0°C . by the aid of a table given on page 248 of Kohlrausch's *Kleiner Leitfaden der Praktischen Physik*.

APPARATUS No. 3.

In order to have a second piece of apparatus available for experiments with ether, so that two experiments could be made at the same time, a third piece of apparatus was constructed. The mercury tube of this apparatus was made a little smaller than that of apparatus No. 2, as some difficulty had been met in the mercury column failing to hold together properly. The capillary of this apparatus was also elliptical and slightly conical. The average semi-major axis as determined by the microscope and mercury was .006176 cm. while the minor axis was .002837. The length of the capillary was 73.25 cm. at first, but was reduced to 70 cm. when the apparatus was repaired after a breakage.

The distance between the marks on the mercury tube was 38.45 cm. and the volume of gas transpired was .742 c.c. since 10.0634 grams of mercury occupied the distance between the marks at 16°C . The average diameter of the mercury tube where the mercury traversed it during an experiment was .158112 cm.

A table of the results obtained with this apparatus for air

is given on page 71 underneath those for air with apparatus No. 2. It will be noticed that the two pieces of apparatus agree very closely in results.

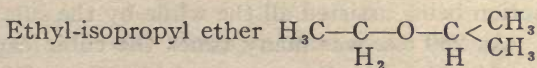
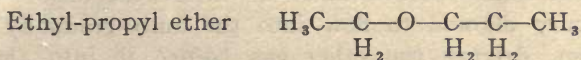
TABLE OF INTERNAL FRICTION OF ETHER GASES.
APPARATUS No. 3.

Length Capillary	Kind of Gas	Temp. of Gas	Ht. of driving Col. at 0° C	Barom. at 0° C	Press of entering Gas	Time in seconds	$\eta \times 10^7$	Average $\eta \times 10^7$
70.	Di-meth-	100.3	18.75	77.24	95.03	315.6	1191.8	1190.2 \pm 1.
70.	yl Ether	100.3	18.74	77.32	95.10	314.8	1188.6	
70.	Ethyl	100.3	18.74	76.98	94.67	303.6	1145.6	1155. \pm 6.3
70.	Alcohol	100.3	18.76	76.99	94.70	308.4	1164.4	
73.25	Di-ethyl	100.1	18.78	76.43	94.26	287.4	1041.8	1001. \pm 8.15
73.25	Ether	100.	18.60	76.15	93.81	287.4	1023.2	
73.25		100.	18.79	76.03	93.88	270.4	978.4	
70.		99.9	18.76	75.80	93.61	254.8	963.7	
70.		100.1	18.56	76.46	94.07	266.5	998.1	
73.25	Ethyl-	99.9	18.76	75.79	93.61	253.2	914.8	918.4 \pm 4.2
73.25	Propyl	99.9	18.26	75.74	93.06	267.2	939.3	
73.25	Ether	100.	18.05	76.39	93.50	262.4	921.7	
73.25		100.3	18.28	76.83	94.16	256.6	902.7	
73.25		100.4	18.05	77.02	94.14	263.2	913.7	
70.	Ethyl-	100.2	17.74	76.46	93.26	267.7	946.4	960.7 \pm 5.
70.	Isopro-	100.2	18.76	76.41	94.22	255.4	966.4	
70.	pyl Ether	100.2	18.56	76.34	93.95	258.8	969.3	
70.	Di-Pro-	100.	18.75	75.95	93.73	222.2	839.5	837.5 \pm 1.26
70.	pyl	100.	18.76	76.02	93.74	222.0	839.3	
70.	Ether	100.3	18.75	77.14	94.93	220.8	832.7	
70.	Isopro-	100.1	18.73	76.19	93.97	230.4	870.2	873.4 \pm 2.2
70.	pyl-pro-	100.1	18.76	76.22	94.03	231.6	876.6	
	pyl Ether							
70.	Di-iso-	100.3	18.74	77.14	94.92	230.2	869.2	894.3 \pm 5.95
70.	propyl	100.3	18.74	77.14	94.92	230.8	871.5	
70.	Ether	100.3	18.76	77.09	94.89	239.0	902.8	
70.		100.3	18.74	77.13	94.91	236.0	890.7	
70.		100.1	18.73	76.23	94.01	241.0	910.5	
70.		100.1	18.75	76.23	94.03	243.6	921.2	

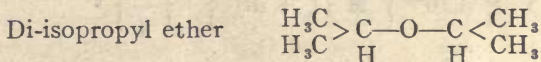
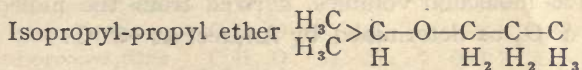
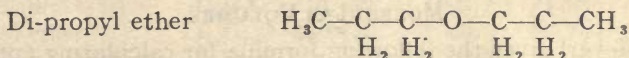
The results obtained for ethers with this apparatus are given in the above table. The first point worthy of note is that ethyl alcohol which is metameric with di-methyl ether has about 3% lower coefficient of friction, showing it to have the larger molecule,

The values for di-ethyl ether, and ethyl-propyl ether agree well with those given on page 43 by apparatus No. 2.

Ethyl-isopropyl ether has a friction 4.6% higher than that of ethyl propyl ether, hence has a smaller molecule.



Isopropyl-propyl ether has a friction 4.3% higher than that of di-propyl ether, while di-isopropyl ether has a friction 6.8% higher than di-propyl. This is in accordance with our view of the concatenation of the atoms in these molecules. Di-propyl ether is a straight, chain compound whereas iso-propyl propyl has two branches and di-isopropyl has four branches.



As already noticed the difference between methyl-propyl and methyl-isopropyl is 5% due to 2 branches; the difference between ethyl-propyl and ethyl-isopropyl due to two branches is 4.6%; the difference between di-propyl and isopropyl-propyl is 4.3 % due to the same number of branches. The diminishing effect of the 2 CH₃ branches is probably due to the fact that the molecules of the substances lower on the lists are larger, hence the branches have a smaller relative effect. It would seem that di-isopropyl ether ought to be 8.6% higher than di-propyl whereas it is only 6.8%. This discrepancy I am unable to explain.

Di-methyl ether, being a gas at ordinary temperatures, had to be handled differently from the other ethers, all of which were put into the apparatus as liquids. The low boiling ethers, methyl-ethyl, and methyl-isopropyl were experimented upon in a room whose temperature was at or very near 0° C.

The di-methyl ether gas was kept in sealed glass bulbs of 250 c.c capacity. The lower end of a bulb was connected by rubber tubing to a reservoir of mercury while the upper end was connected by a rubber tube to the funnel at the top of the apparatus.

After the aspirator had created a partial vacuum in the apparatus by sucking the air out through the capillary, the tips of the bulb were broken off inside the rubber tubes and mercury allowed to flow into the bulb gradually from the bottom, driving the ether gas before it into the apparatus, the action being assisted all the while by the suction of the aspirator. As 250 c.c. was many times the cubic capacity of the apparatus, by the time the mercury had entirely filled the ether bulb, it was judged the apparatus would be filled with pure ether, unmixed with any air. This method of getting the ether gas into the apparatus proved a failure several times for various reasons, but the very close agreement of the two readings which were at length obtained points to their correctness.

MOLECULAR VOLUMES.

L. Meyer¹ gives the following formula for calculating approximate relative molecular volumes, derived from the molecular volume of $S O_2$ as determined by Andreef at $-8^\circ C$

$$V = 3.10^{-6} \left\{ M (1 + \alpha t) \right\}^{\frac{2}{3}} \left\{ \frac{1}{\eta} \right\}^{\frac{2}{3}}$$

in which M = molecular weight, t = temperature centigrade η = coefficient of friction.

The values obtained for the substances under investigation are given on the next page. According to Kopp¹ the molecular volume of a liquid composed of carbon, hydrogen and oxygen can be found by substituting in its formula 11 for each atom of carbon, 5.5 for each hydrogen and 7.8 for each oxygen. The values thus calculated are given in the last column. The agreement between the molecular volumes calculated in these two ways is quite good, much better than that obtained by L. Meyer and Schumann (p. 21).

As both apparatus No. 2 and No. 3 gave values for air about 5% higher than those given by Landolt and Boernstein as probably the most correct values, it is probable that the values of η for the ethers are correspondingly too high. Accordingly in the second table of molecular volumes the values of η were reduced by multiplying by 2113/2244, thus calibrating with air, and the molecular volumes recalculated. A still better

1. Wied. Ann., 1881, Bd. 13, p. 17.

1. Ann. Chem. Phar., 1855, Bd. 96, pp. 1, 153, 303.

agreement with Kopp's values is shown, the disagreement being greatest when the boiling point of the ether approaches the temperature at which η was determined.

FIRST TABLE OF MOLECULAR VOLUMES.

Material	Formula	Boiling Point Cent.	$\eta \times 10^7$	Molec. V. Found	Molec. V. Calculated according to Kopp
Di-methyl ether	C_2H_6O	-23.65	1190.2	51.62	62.8
Ethyl alcohol	C_2H_6O	78.	1155.0	55.25	
Methyl-ethyl ether	C_3H_8O	10.-13.	1092.3	71.65	84.8
Di-ethyl ether	$C_4H_{10}O$	34.6-35.	1000.	95.73	
Methyl-propyl ether	$C_4H_{10}O$	40-45.	1004.3	95.16	106.8
Methyl-isopropyl ether	$C_4H_{10}O$	7.	1054.8	88.37	
Ethyl-propyl ether	$C_5H_{12}O$	66.-68.	916.8	124.19	128.8
Ethyl-isopropyl ether	$C_5H_{12}O$	54.-57.	960.7	115.77	
Di-propyl ether	$C_6H_{14}O$	84.5-86.5	837.5	158.90	150.8
Isopropyl-propyl-ether	$C_6H_{14}O$	76.5-77.	873.4	148.86	
Di-isopropyl ether	$C_6H_{14}O$	68.5-69.	894.3	144.06	

SECOND TABLE OF MOLECULAR VOLUMES.

Material	Formula	Boiling Point in deg. Cent.	$\eta \times 10^7$	Molec. V. Found	Molec. V. Calculated according to Kopp
Di-methyl ether	C_2H_6O	-23.65	1121.0	56.46	62.8
Ethyl alcohol	C_2H_6O	78.	1088.0	59.05	
Methyl-ethyl ether	C_3H_8O	10.-13.	1029.0	81.12	84.8
Di-ethyl ether	$C_4H_{10}O$	36.6-35.	942.0	104.71	
Methyl-propyl ether	$C_4H_{10}O$	40.-45.	946.0	104.20	106.8
Methyl-isopropyl ether	$C_4H_{10}O$	7.	993.6	96.66	
Ethyl-propyl ether	$C_5H_{12}O$	66.-68.	863.6	135.84	128.8
Ethyl-isopropyl ether	$C_5H_{12}O$	54.-57.	905.1	126.61	
Di-propyl ether	$C_6H_{14}O$	84.5-86.5	788.9	173.08	150.8
Isopropyl-propyl-ether	$C_6H_{14}O$	76.5-77.	822.7	163.20	
Di-isopropyl ether	$C_6H_{14}O$	68.5-69.	842.4	157.51	

In this second table η has been reduced by calibration with air.

MOLECULAR MEAN SPEEDS, FREE PATHS AND COLLISION FREQUENCIES.

In Meyer's Kinetic Theory of Gases on page 219 is given the formula $\eta = 0.30967 \rho L \Omega$ whence

$$L = \frac{\eta}{0.30967 \rho \Omega}$$

in which η = coefficient of internal friction of the gas

ρ = density of the gas

Ω = mean molecular velocity

L = mean molecular free path.

On page 55 of the same work we find $p = \frac{1}{8} \pi \rho \Omega^2$ whence

$$\Omega = \sqrt{\frac{8p}{\pi \rho}}$$

where p = pressure in absolute measure.

On page 195 we see that the

$$\text{Collision Frequency} = \frac{\Omega}{L}$$

The values given in the table on this page were calculated according to the above formulae, at a pressure of 76 cm. of mercury and a temperature of 100°C., the density being calculated from the formula

$$\rho = 1/2 \frac{(\text{formula weight}) (0.000089)}{1 + \alpha t.}$$

It will be noticed that the values are all of the proper order of magnitude, but do not rise and fall in a periodic way while the

FIRST TABLE OF MEAN MOLECULAR SPEEDS, FREE PATHS AND COLLISION FREQUENCIES.

Material	Molecular Weight	$\eta \times 10^7$	Mean Molecular speed cm. per sec.	Molecular Free Path $\times 10^{10}$	Collision Frequency $\times 10^{-6}$
Di-methyl ether	46.048	1190.2	41470	61787	6711.7
Ethyl alcohol	46.048	1155.0	41470	59970	6915.0
Methyl-ethyl ether	60.064	1092.3	36310	49660	7312.0
Di-ethyl ether	74.08	1000.0	32695	40895	7994.9
Methyl-propyl ether	74.08	1004.3	32695	41111	7952.7
Methyl-isopropyl ether	74.08	1054.8	32695	43180	7572.0
Ethyl-propyl ether	88.096	916.8	29982	34415	8711.8
Ethyl-isopropyl ether	88.096	960.7	29982	36063	8315.5
Di-propyl-propyl ether	102.112	837.5	27848	29201	9536.6
Isopropyl-propyl ether	102.112	873.4	27848	30454	9144.6
Di-isopropyl ether	102.112	894.3	27848	31182	8931.0

SECOND TABLE OF MEAN MOLECULAR SPEEDS, FREE PATHS AND COLLISION FREQUENCIES.

Di-methyl ether	46.048	1121.0	41470	58204	7125.0
Ethyl alcohol	46.048	1088.0	41470	56490	7341.0
Methyl-ethyl ether	60.064	1029.0	36310	46782	7762.0
Di-ethyl ether	74.08	942.0	32695	38570	8477.0
Methyl-propyl ether	74.08	946.0	32695	38725	8639.5
Methyl-isopropyl ether	74.08	993.6	32695	40682	8036.7
Ethyl-propyl ether	88.096	863.6	29982	32418	9248.4
Ethyl-isopropyl ether	88.096	905.1	29982	33976	8824.3
Di-propyl propyl ether	102.112	788.9	27848	27507	10124.0
Isopropyl-propyl ether	102.112	822.7	27848	28685	9708.0
Di-isopropyl ether	102.112	842.4	27848	29372	9481.1

In this second table η has been reduced by calibration with air.

molecular weight increases, as pointed out for other substances by Meyer on page 196 of his Kinetic Theory of Gases, probably because these ethers are all so closely related.

COMPARISON WITH THE RESULTS OF OTHERS.

The results of my work cannot be compared satisfactorily and exactly with that of others, because I have determined the friction at a temperature higher than most other observers, and the law of its increase with the temperature is not accurately known in each case. Furthermore, air, di-ethyl ether, dimethyl ether and ethyl alcohol are the only substances which I have employed that others have investigated.

Disregarding the results with apparatus No. 1 as being only preliminary, we see that the values of η for air for the other two pieces of apparatus agree closely and are consistent, though both are about 5% higher than the values which are most probably correct, according to Landolt and Boernstein's tables. That the relative values of η at the different temperatures are correct is shown by calculating η at 0° C. by Sutherland's formula (see page 30) and then calculating from that η at 100° C. Using the value of the cohesion constant $C=119.4$ as determined by Breitenbach we get for apparatus No. 2, $\eta_0 = .0001793$ and $\eta_{100} = .00022367$ the latter value agreeing with .0002242 observed within 1/4%. For apparatus No. 3 we get in like manner $\eta_0 = .0001795$ and $\eta_{100} = .0002239$, the latter value agreeing with .0002246 observed within 1/4%. This agreement is within the limits of error of the experiments.

Puluj's formula for the coefficient of friction of di-ethyl ether vapor, $\eta = 0.0000689 (1 + .0041575 t)^{.04}$ gives $\eta = 0.0000935$ at 100°C. which agrees with my corrected value of 0.0000942 within $\frac{3}{4}\%$. This is good agreement bearing in mind the fact that Puluj's formula was determined from experiments over a small range of temperature, viz.: from 0° to 37°C.

The coefficient of friction of di-methyl ether is given on page 192 of Meyer's Kinetic Theory of Gases as 0.000092 at 0°C. No one has determined the law of its increase with the temperature. My corrected value is $.0001121$ at 100°C. which seems reasonable.

Steudel (see page 21) gives 0.000142 as the coefficient of friction of ethyl alcohol at 78.4°C. , its boiling point. My corrected value of $.0001088$ at 100°C. does not agree well with this. Because his value was determined at the boiling point I think it is open to question. My value for ethyl alcohol agrees much better with Puluj's¹ results which are 0.0000827 at 0°C. and 0.0000885 at 16.8°C. He assumes η is proportional to the absolute temperature which gives $\eta = .0001130$ at 100°C. , which is nearly 4% higher than my value of $.0001088$. I think the assumption that η increases exactly as the absolute temperature is not strictly correct.

Concerning the differences which I have found between the normal propyl and the iso-propyl ethers I would point out that Lothar Meyer, Schumann and Steudel (see pages 20 to 23) found similar differences between many, though not all, of the normal propyl and iso-propyl compounds which they examined. They also found that normal butyl, isobutyl and tertiary butyl compounds showed still more regular differences. The weight of evidence gives a larger molecule to the primary, a smaller to the secondary and the smallest to the tertiary compound. My values of the molecular speeds, free paths and collision frequencies being for 100°C. of course do not agree with those calculated for 0°C. by others.

SUMMARY OF RESULTS.

1. A new and simple apparatus for determining the internal friction of gases and vapors has been developed.
2. The coefficients of internal friction of the following eight ether gases which have hitherto not been experimented with, have been determined with considerable accuracy as follows:

Methyl-ethyl ether.....	0.0001029	at 100° C.
Methyl-propyl ether.....	0.0000946	" "
Methyl-isopropyl ether.....	0.00009936	" "
Ethyl-propyl ether.....	0.00008636	" "
Ethyl-isopropyl ether.....	0.00009051	" "
Di-propyl ether.....	0.00007889	" "
Iso-propyl-propyl ether.....	0.00008227	" "
Di-isopropyl.....	0.00008424	" "

3. The molecular volumes calculated from the friction have been shown to agree fairly well with those obtained by Kopp's rule.

4. A marked and unmistakable difference between the normal propyl and isopropyl ethers has been found, proving that the difference in the molecular structure of these ethers has a very noticeable effect upon their internal friction, and therefore upon the size of their molecules, the molecules having the most numerous branches being smaller than those with fewer or no branches. The object of this research has therefore been accomplished.

In conclusion I wish to express my most sincere and heartfelt thanks to Professor Loeb for suggesting to me both the subject of this research and the form of apparatus, and for his kind interest and help throughout the course of the investigation. In addition I wish to thank him heartily for his very great courtesy in supplying me with the necessary ethers.

I also wish to express my thanks to Professors Charles Baskerville and Charles A. Doremus of the College of the City of New York, for their kindness in permitting me to perform most of the experiments in the chemical laboratory of that institution, in order to save time in going to and from the laboratory of New York University.

FREDERICK M. PEDERSEN.

New York University, April, 1905.

BIBLIOGRAPHY.

BAILY.

Phil. Trans., 1832, p. 399.

BARUS.

Am. Journ. Sci., 1888 (3), Vol. 35, p. 407.

Bull. U. S. Geol. Survey, No. 54, Washington, 1889, p. 39.

Wied. Ann., 1889, Bd. 36, p. 358.

Phil. Mag., 1890, Vol. 29, p. 337.

BERNOULLI, JOHANN.

Opera omnia. Lausannae et Genevae, 1742, Tomus III. Nouvelles pensées sur le système de M. Descartes XIX.-XXIII.

BESSEL.

Abh. d. Berl. Akad. Math. Klasse, 1826, p. 1.

BESTELMEYER.

Inaug. Diss. Munich, 1902.

Ann. d. Phys., 1904, Vol. 13, p. 944.

BOLTZMANN.

Wien. Ber. Math. Naturw., 1868, Bd. 58 (2), p. 517.

“ “ “ “ 1872, “ 66 (2), p. 324.

“ “ “ “ 1880, “ 81 (2), p. 117.

“ “ “ “ 1881, “ 84 (2), pp. 40, 1230.

“ “ “ “ 1887, “ 95 (2), p. 153.

“ “ “ “ 1888, “ 96 (2), p. 891.

Wied. Ann., 1897, Bd. 60, p. 399.

BRAUN AND KURZ.

Carls Rep., 1882, Vol. 18, pp. 569, 665, 697.

“ “ 1883, Vol. 19, pp. 343, 605.

BREITENBACH.

Wied. Ann., 1899, Bd. 67, p. 803.

Ann. d. Phys., 1901, Bd. 5, p. 166.

CAUCHY.

Exerc. de Mathém., 1828, p. 183.

CHALLIS.

Phil. Mag., 1833, p. 185.

CHÉZY.

Mém. Manuscript de l'Ecole des Ponts et Chaussée, 1775.

CLAUSIUS.

Pogg. Ann., 1858, Bd. 105, p. 239.

CLEBSH.

Crelle's Journ. für Math., Bd. 52, 1856, p. 119.

COUETTE.

Compt. Rend., 1888, Vol. 107, p. 388.

Journ. de Phys., 1890 (2), Vol. 9, p. 414.

Ann. de Chim. et de Phys., 1890 (6), Vol. 21, p. 433.

COULOMB.

Mém. de l'Institut National. Year 9 (1801), Tome III., p. 246.

COUPLET.

Mém. de l'Académie, 1732.

CROOKES.

Phil. Trans., 1881, Vol. 172, p. 387.

D'ALEMBERT.

Traité de l'équilibre et du mouvement des fluides, nouvelle édit.
Paris, 1770.

D'ARCY.

Mém. de Divers Savans, 1858, Vol. 15, p. 141.

DE HEEN.

Bull. de l'Acad. de Belgique, 1888 (3), Vol. 16, p. 195.

DU BUAT.

Principes d'Hydraulique, 1786.

EULER.

Tentamen theoriae de frictione fluidorum. Novi commentarii Pteropolitani, tomus VI., 1756, et 57 Pag. 338. Die Gesteze des Gleichgewichtes und der Bewegung flüssiger Körper. Translated from the Latin by W. Brandes. Leipzig, 1806.

EYTELWEIN.

Abh. d. Berl. Akad., 1814 and 1815.

GERSTNER.

Neu. Abh. der kön. Böhmischen Gesell. der Wiss., Bd. 3, Prag 1798.
Gilbert's Annalen, Bd. 5, 1900, p. 160.

GIRARD.

Mém. de l'Institut., Classe Sc. Math., 1813-15, p. 248; 1816, p. 187

GIRAULT.

Mém. de l'Acad. de Caën, 1860.

GIULIO.

Memorie di Torino, Ser. 2, tomo 13, 1853.

GRAHAM.

Phil. Trans., 1846, Vol. 136, pp. 573, 622.

" " 1849, Vol. 139, p. 349.

Pogg. Ann., 1866, Bd. 127, pp. 279, 365.

GREEN.

Transactions of the Royal Society of Edinburgh, 1836, Vol. 13, p. 54.

GRONAU.

Über die Bewegung schwingender Körper im widerstehenden Mittel.
Danzig, 1850.

Program der Johannesschule.

GROSSMAN.

Inaug. Diss. Breslau, 1880.

Wied. Ann., 1882, Bd. 16, p. 619.

GROTRIAN.

Pogg. Ann., 1876, Vol. 157, pp. 130, 237.

" " 1877, Vol. 160, p. 238.

Wied. Ann., 1879, Vol. 8, p. 529.

GUTHRIE.

Phil. Mag., 1878 (5), Vol. 5, p. 433.

HAGEN.

Pogg. Ann., 1839, Bd. 46, p. 423.

Abth. d. Berl. Akad., 1854, p. 17.

HAGENBACH.

Pogg. Ann., 1860, Bd. 109, pp. 385, 401.

HELMHOLTZ AND PIETROWSKI.

Wien. Ber. Mathem. Naturw., 1860, Vol. 40, p. 607.

HOFFMANN.

Wied. Ann., 1884, Bd. 21, p. 470.

HOLMAN.

Proc. Am. Acad. Boston, 1877, Vol. 12, p. 41.

“ “ “ “ 1886, Vol. 21, p. 1.

Phil. Mag., 1877 (5), Vol. 3, p. 81; 1886, Vol. 21, p. 199.

HOUDAILLE.

Fortschr. d. Phys., 1896, 52 Jahr., I., p. 442.

JACOBSON, H.

Archiv. für Anatomie und Physiologie von Reichert und Du Bois
1860 and 1861.

JAEGER.

Wien. Ber. Mathm. Naturw., 1899 (2), Vol. 108, p. 447.

“ “ “ “ 1900 (2), Vol. 109, p. 74.

JOB.

Bull. Soc. Franc. Phys., 1901, Vol. 157, p. 2.

KLEMENCIC.

Carls. Rep., 1881, Bd. 17, p. 144.

Wien. Ber., 1881 (2), Bd. 84, p. 146.

Beiblätter, 1882, Bd. 6, p. 66.

KIRCHHOFF.

Mechanik., 1877, 4 Aufl., 26 Vorl., p. 383.

KOCH.

Wied. Ann., 1883, Bd. 19, p. 857.

KOENIG.

Wied. Ann., 1885, Bd. 25, p. 618; 1887, Bd. 32, p. 193.

Sitz. d. Münch. Akad., 1887, Bd. 17, p. 343.

KUNDT AND WARBURG.

Monatsber. d. Berl. Akad., 1875, p. 160.

Pogg. Ann., 1875, Vol. 155, pp. 337, 525.

Phil. Mag., 1875 (4), Vol. 50, p. 53.

KLEINT.

Inaug. Diss. Halle, 1904.

LAMPE.

Programm des Stadtischen Gym. zu Danzig, 1866.

LAMPEL.

Wien. Ber. Mathem. Naturw., 1886, Bd. (2), p. 291.

LANG.

Wien. Ber. Math. Naturw., 1871, Vol. 63 (2), p. 604.

“ “ “ “ 1872, Vol. 64 (2), p. 487.

Pogg. Ann., 1872, Vol. 145, p. 290.

“ “ 1873, Vol. 148, p. 550.

LUDWIG AND STEFAN.

Sitzber. Wien. Akad., 1858, Vol. 32, p. 25.

MARIAN.

Histoire de l'Acad. de Paris, 1735, p. 166.

MARGULES.

Wien. Ber. Mathem. Naturw., 1881, Vol. 83 (2), p. 588.

MARKOWSKI.

Inaug. Diss. Halle, 1903.

Ann. d. Phys., 1904, Vol. 14, p. 742.

MAXWELL.

Phil. Mag., 1860 (4), Vol. 19, p. 31.

" " 1868 (4), Vol. 25, p. 209 and 211.

Phil. Trans., 1866, Vol. 156 (1), p. 249.

Collected Papers, Vol. II.

Proc. Royal Society, 1866, Vol. 15, p. 14.

MATHIEU.

Compt. Rend., 1863, Tome 57, p. 320.

MEYER, LOTHAR.

Ann. d. Chem. u. Phar., 1867, Suppl. Bd. 5, p. 129.

Wied. Ann., 1879, Bd. 7, p. 497.

" " 1882, Bd. 16, p. 394.

MEYER, L. AND SCHUMANN.

Wied. Ann., 1881, Bd. 13, p. 1.

MEYER, O. E.

Dissertation: de mutua duorum fluidorum frictione.

Regimonti's Prussorum, 1860.

Crelle's Journal für Mathem., 1861, Bd. 59, p. 229.

Pogg. Ann., 1861, Bd. 113, p. 55; 1865, Bd. 125, pp. 177, 401, 564;
1866, Bd. 127, pp. 253, 353; 1871, Bd. 142, p. 513; 1871, Bd. 143,
p. 14; 1873, Bd. 148, p. 203.

Wied. Ann., 1887, Bd. 32, p. 642; 1891, Bd. 43, p. 1.

Sitz. d. München Akad., 1887, Bd. 17, p. 343.

MEYER, O. E. AND SPRINGMÜHL.

Pogg. Ann., 1873, Vol. 148, p. 526.

MORITZ.

Pogg. Ann., Bd. 70, p. 74.

MÜTZEL.

Wied. Ann., 1891, Bd. 43, p. 15.

NAUMANN.

Ann. d. Chem. u. Pharm., 1867, Suppl. Bd. 5, p. 252.

NAVIER.

Mém. de l'Acad. des Sciences, 1823, Tome 6, p. 389.

" " " " " 1830, Tome 9, p. 311.

NOYES AND GOODWIN.

Physical Review, 1896, Vol. 4.

Zeitsch. Physik. Chem., 1896, Vol. 21, p. 671.

NEUMANN.

Einl. in d. theor. Physik., 1883, p. 246.

NEWTON.

Philosophiae naturalis principia mathematica, 1687, Lib. II., Sect. IX.

OBERMAYER.

- Wien. Ber. Mathem. Naturw., 1875, Vol. 71 (2), p. 281.
 " " " " 1876, Vol. 73 (2), p. 433.
 Carls. Rep., 1876 (2), Vol. 12, pp. 13, 456.
 " " 1877, Vol. 13, p. 130.
 Phil. Mag., 1886, Vol. 21.

ORTLOFF.

- Inaug. Diss. Jena, 1895.

PÉROT AND FABRY.

- Compt. Rend., 1897, Vol. 124, p. 28.
 Ann. de Chim. et de Phys., 1898 (7), Vol. 13, p. 275.

POISEUILLE.

- Soc. Philomath, 1838, p. 77.
 Compt. rend., 1840, Vol. 11, pp. 961, 1041.
 1841, Vol. 12, p. 112.
 1842, Vol. 15, p. 1167.
 Ann. de Chim. et de Phys., 1843 (3), Vol. 7, p. 50.
 Mém. de Savans étrangers. 1846, Vol. 9, p. 433.

POISSON.

- Journal de l'Ecole Polytech., 1831, 20 me cahier, tome 13, p. 139.
 Connaissance des Temps, 1834. Appendix.
 Mém. de l'Acad., Tome 2, 1832, p. 521.

PLANA.

- Mém. de l'Acad. di Torino, T 37, 1835.

PRONY.

- Recherches physico-mathématiques sur la théorie des eaux courantes.
 Paris, 1804.

PULJ.

- Wien. Ber. Mathem. Naturw., 1874, Bd. 69 (2), p. 287.
 " " " " 1874, Bd. 70 (2), 243.
 " " " " 1876, Bd. 73 (2), 589.
 " " " " 1878, Bd. 78 (2), p. 279.
 Carls. Rep., 1878, Bd. 14, p. 573.
 " " 1879, Bd. 15, pp. 427, 578, 633.
 Phil. Mag., 1878 (5), Vol. 6, p. 157.

RAYLEIGH.

- Proc. Roy. Soc., 1900, Vol. 66, p. 68; Vol. 67, p. 137

RELLSTAB.

- Inaug. Diss. Bonn., 1868.

REYNOLDS, F. G.

- Phys. Rev., 1904, Vol. 18, p. 419; Vol. 19, p. 37.

REYNOLDS, O.

- Proc. Roy. Inst. Grt. Brit., 1884, Vol. 11, p. 44.
 Beiblätter, 1886, Bd. 10, p. 217.

SABINE.

- Phil. Trans., 1829, p. 207 and 331; 1831, p. 470.

SCHNEEBELI.

- Arch. de Genève, 1885, Vol. 14 (3), p. 197.

SCHULTZE.

- Ann. d. Physik., 1801, Bd. V., p. 140.

SCHUMACHER.

Astronomische Nachrichten, Bd. 40, 1855.

SCHUMANN.

Wied. Ann., 1884, Bd. 23, p. 353.

STEFAN.

Wien. Ber. Mathem. Naturw., 1862 (2), Vol. 46, pp. 8, 495.

" " " " 1872 (2), Vol. 65, p. 360.

STEUDEL.

Wien. Ann., 1882, Bd. 16, p. 369.

STEWART AND TAIT.

Proc. Royal Society, 1865, Vol. 14, p. 339.

Phil. Mag. (4), Vol. 30, p. 314.

STOKES.

Camb. Phil. Trans., 1849, Vol. 8, p. 287.

" " " 1850, Vol. 9, p. 8.

Phil. Mag., 1851 (4), Vol. 1, p. 337.

ST. VENANT, BARRÉ DE.

Compt. Rend., 17, 1843, pp. 1140 and 1240.

SUTHERLAND.

Proc. Ann., Acad. 1885, p. 13.

Phil. Mag., 1893 (5), Vol. 36, p. 507.

TOMLINSON.

Phil. Trans., 1886, Vol. 177 (2), p. 767.

WARBURG.

Pogg. Ann., 1876, Bd. 159, p. 399.

WARBURG AND BABO.

Wied. Ann., 1882, Bd. 17, p. 390.

Sitz. d. Berl. Akad., 1882, p. 509.

WIEDEMANN, G.

Pogg. Ann., 1856, Bd. 99, p. 177.

WIEDEMANN, E.

Arch. d. Sc. Phys. et Nat. de Genève, 1876, Vol. 56, p. 277.

Fortschr. d. Phys., 1876, Vol. 32, p. 206.

THIS BOOK IS DUE ON THE LAST DATE
STAMPED BELOW

AN INITIAL FINE OF 25 CENTS
WILL BE ASSESSED FOR FAILURE TO RETURN
THIS BOOK ON THE DATE DUE. THE PENALTY
WILL INCREASE TO 50 CENTS ON THE FOURTH
DAY AND TO \$1.00 ON THE SEVENTH DAY
OVERDUE.

APR 21 1937

19 Sep '60 MM

REC'D LD

SEP 19 1960

LD 21-100m-8,'34

QL175

P4

239372

Pedersen

